Novel Possibilities in Chemical Pretreatment and Finishing of Cotton Fabrics

Dissertation

zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften
– Dr. rer. nat. –

vorgelegt von

Vahid Ameri Dehabadi
geboren in Kashan/Iran

Institut für Deutsches Textilforschungszentrum Nord-West gGmbH
der
Universität Duisburg-Essen

2012

Die vorliegende Arbeit wurde im Zeitraum von Nov 2008 bis Juli 2012 im Arbeitskreis von Prof. Dr. Gutmann am Institut für Deutsches Textilforschungszentrum Nord-West gGmbH der Universität Duisburg-Essen durchgeführt.

Tag der Disputation: 10.12.2012

Gutachter:	Prof. Dr. Gutmann
	Prof. Dr. Ulbricht
Vorsitzender:	Prof. Dr. Spohr

Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit mit dem Titel

„Novel Possibilities in Chemical Pretreatment and Finishing of Cotton Fabrics ”

selbst verfasst und keine außer den angegebenen Hilfsmitteln und Quellen benutzt habe, und dass die Arbeit in dieser oder ähnlicher Form noch bei keiner anderen Universität eingereicht wurde.

Essen, im Juli 2012

Vahid Ameri Dehabadi

Novel Possibilities in Chemical Pretreatment and Finishing of Cotton Fabrics

Von der Fakultät für Chemie
der Universität Duisburg-Essen

zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften

genehmigte Dissertation

von

Vahid Ameri Dehabadi

Essen–Deutschland

Juli 2012

Acknowledgment

I am heartily thankful to my supervisor Prof. Dr. Jochen Stefan Gutmann, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject.

I also must declare my specially thanks to retired Prof. Dr. Eckhard Schollmeyer, who had kindly helped and let me to continue my study in University of Duisburg-Essen.

I owe my deepest gratitude to Dr. Hans-Jürgen Buschmann and Dr. Klaus Opwis, who without their support, patience and guidance this study would not have been completed.

I am indebted to many of my colleagues in *Deutsches Textilforschungszentrum Nord-West e. V.* to support me during completion of this project: Dr. Reiner Benken, Dr. Dirk Knittel, Dr. Torsten Textor, Dr. Thomas Mayer-Gall, Harald Fink, Ulrike Artz, Andrea Fischer, Leonie Derksen and Elke Roskothen.

And finally, I would like to thank my dear wife, Nazanin, for her understanding and endless love, my family, specially my mother, who are not by my side but their warm encouragements from a long distance, my home country, always warm me up to overcome the challenge in my studies and my dear friends Habib Shalchian, Abbas Aghaei and Kamal Arass.

Vahid Ameri Dehabadi

To:

my love Nazanin,

my mother,

&

my father, whose memory is always with me

Table of Contents

List of Figures

List of Tables

List of Equations

Abstract

Chemical or wet processing of textiles can be basically divided to three stages: pretreatment, dyeing and finishing. Raw cotton fibers have to be treated through several chemical, physical and biological processes before dyeing to obtain desirable properties and become suitable for use or for further treatments. These processes are known as “pretreatment processes”. The aim of the cotton pretreatment is to remove the undesired substances from raw cotton, which are brought to material in the form of natural and process-related attendant substances, by application of processes such as singeing, desizing, scouring and bleaching. Finishing provides extra properties for textiles that customers will value. In the other word, finishing is completing the fabric’s performance by providing special functions. The most conventional and important chemical finishing processes are: softening finishing, hand building finishing, easy-care and durable press finishing of cellulosic fabrics, repellent finishing, soil-release finishing, flame retardant finishing, non-slip finishing, antistatic finishing, anti-pilling finishing, elastomeric finishing, ultraviolet protection finishing, antimicrobial finishing, insect resist and mite protection finishing and etc.

The main trend of development in chemical processes of textiles is shortening and simplification of pretreatment processes through combination of two or more stages. The important processes, such as desizing, scouring and bleaching are usually carried out in separate stages in the conventional pretreatment processes. Also consumption of large amount of energy and water is the other aspect of the conventional preparation of textiles. It has been already known that, to minimize the energy and water consumption the combination of several stages of the pretreatment processes by lowering the number of operations or reducing the time of reaction is absolutely necessary. Also, textile industry tends to utilize combination of the finishing processes in a single bath or at least reducing number of the necessary stages to decrease the costs of production. Using multifunctional finishing seems as one of the most attractive fields in textile industry. This idea has

been investigated by some researchers to provide more effects in a finished fabric just in a single bath.

In this study, it has been tried to combine some important pretreatment processes of cotton fabric by means of enzymes and also create several finishing effects on the cotton fabric through a novel multifunctional finishing process. Thus, the first part of this study has been dedicated to prove the possibility of simultaneous acid-demineralization and enzymatic desizing of cotton fabric in acidic conditions (pH 2) by using industrial acid stable enzymes. Acid-demineralization is necessary to remove undesired cationic metals and earth alkalis. The obtained results show that by use of a mixture of two appropriate enzymes, a glucoamylase (Multifect GA 10L) and an a-amylase (Optisize Next) in a solution of citric acid and presence of a chelating agent, enzymatic desizing, and acid-demineralization is successfully carried out at the same time. Therefore, two processes of pretreatment are integrated into a single process, which effectively reduce time and costs for textile industry.

In the second part, multifunctional finishing of cotton through synthesis and employment of a novel polycarboxylic acid was studied to produce a fabric with several functional properties: easy-care, flame retardant and antimicrobial; without any extra finishing process. By this way, it is possible to combine three separate finishing processes into a single stage. This goal is achieved by carboxylation of polyvinylamine (PVAm), resulting to form a polyamino carboxylic acid as a novel polycarboxylic acid. This product was used for crosslinking of cotton fabric by pad-dry-cure process. The reaction between the carboxylic groups of polyamino carboxylic acid and the hydroxyl groups of cellulose in cotton forms ester links. It makes durable press effect, reduces the flammability of treated cotton and creates biostatic properties. Moreover, due to presence of free amino groups the treated cotton with the polyamino carboxylic acid improves dyeability of cotton with reactive dyes and enables a salt-free dyeing process.

1

Combination of Acid-Demineralization and Desizing of Cotton Fabrics by Using Acid-Stable Starch-Converting enzymes

1.1 Introduction

Cotton fiber has excellent properties such as higher water absorbency and moisture regain. It is comfortable to wear and easy to dye and chemical finishing. Therefore, cotton is almost the most important (natural) fiber used in textiles and apparel (Karmakar, 1999; Arumugam, 2005).

Raw cotton fibers have to be treated through several chemical, physical and biological processes before dyeing to obtain desirable properties and become suitable for final use or for further treatments. These processes are known as "pretreatment processes". The aim of cotton pretreatment is to remove the undesired substances from raw cotton, which are brought to material in the form of natural and process-related attendant substances, by application of processes such as singeing, desizing, scouring and bleaching (Presa & Tavcer 2009; Rouette 2001). The conventional cotton pretreatments are summerized in Figure 1.1.1.

Bleaching is one of the pretreatment processes applied on the cotton fabric. There are different ways for bleaching of cotton. However, peroxide bleaching of cotton and the other natural fibers is the most common bleaching process. The presence of trapped earth alkalis and cationic metal particles in cotton fabric such as calcium, iron, copper, etc. can catalyze the decomposition of perhydroxy anions to molecular oxygen and water during peroxide bleaching. The molecular oxygen has no bleaching function and uncontrolled decomposition of peroxide in contact with cotton will lead to catalytic damage (Kokot & Jermini, 1994a; Kokot et al. 1994b). The mechanism and significance of catalytic damage during peroxide bleaching have been already studied and reported (Trieselt, 1970; Meyer, et al. 1987). The extent of the catalytic damage may be different and depends on concentration of cationic metals (Hebeish et al. 2001). Furthermore, different kinds of cotton with variable metal content can be treated in finishing processes and consequently confronting more problems is expected (Karmakar, 1999; Wieprecht, et al. 2007).

Acid-demineralization which is used in knitted fabrics has not been yet applied in the pretreatment of woven cotton fabrics. This is due to that removing cationic

metals and alkalis by acid demineralization in woven fabric requires an additional stage, which increases the total time and costs of production. Direct application of acid-demineralization for the sized cotton is not suggested, because presence of the sizing agent (mainly starch) on warp yarns can make an undesirable impact on efficiency of demineralization.

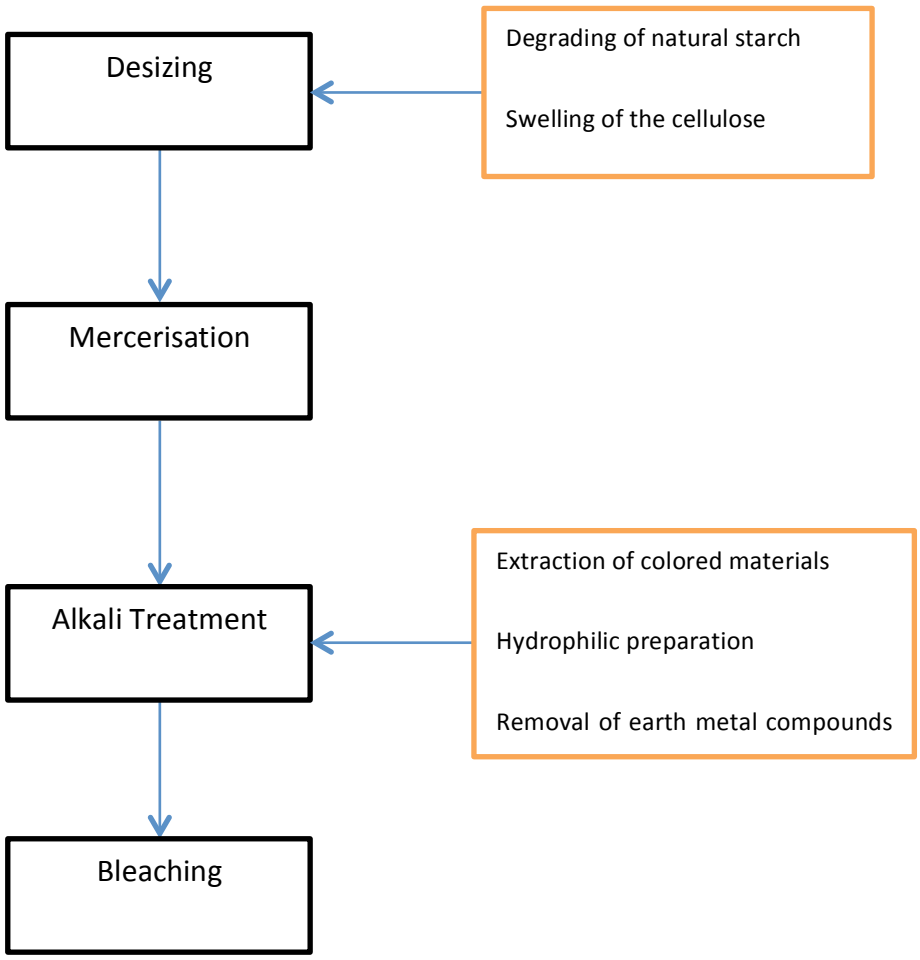

Figure 1.1.1 Pretreatment of cotton fabrics (Rouette 2001)

On the other hand, in the textile industry large amounts of water, energy and auxiliary chemicals are consumed. Especially waste water from the desizing process causes environmental problems (Fukuda et al. 2008). The sizing process is necessary to prevent abrasion, fluffiness and cutting of warp during the weaving process, meanwhile the sizing agent (mainly starch) has negative impact in following treatments, specially dyeing. Therefore, after completion of weaving, sizing agent must be removed. In conventional desizing of cotton fabric, a large amount of hot water, surfactants and the other chemical have to be consumed. To minimize the consumption of water, chemical, energy and also environmental pollution, enzymatic desizing of cotton by amylases has been developed (Feitkenhauer et al. 2003; Mori et al. 1997). Enzymatic desizing was the first use of enzymes in the chemical pretreatment of textiles.

Biotechnology as an ecological advantageous and moreover economical beneficial technology plays an increasingly important role in the industrial wet textile pretreatment and the finishing processes. Due to ever-growing costs of energy and concerning of environmental pollution, enzymatic technologies will stay in the focus of science and technique. While conventional wet textile processes are characterized by long residence time, high concentration of chemicals, alkaline or acidic pH and high temperature, biotechnology is a flexible and reliable tool that presents a promising technology for fulfilling the expected future requirements (Festel et al. 2004; Opwis et al. 2007; Opwis et al. 1999).

1.2 State of research

1.2.1 Structure of cotton

Cotton grows as unicellular fibers on seeds. The cross section of a cotton fiber consists of a number of concentric layers. They can be broadly classified as belonging to either the outermost region called the primary wall or the inner region designated as the secondary wall. The surface properties of cotton fibers are largely the result of cellulosic structure plus a waxy material covering and impregnating

this cellulosic structure. Figure 1.2.1 illustrates the structure of cotton (Arumugam, 2005; Wakelyn & Betroniere , 2007).

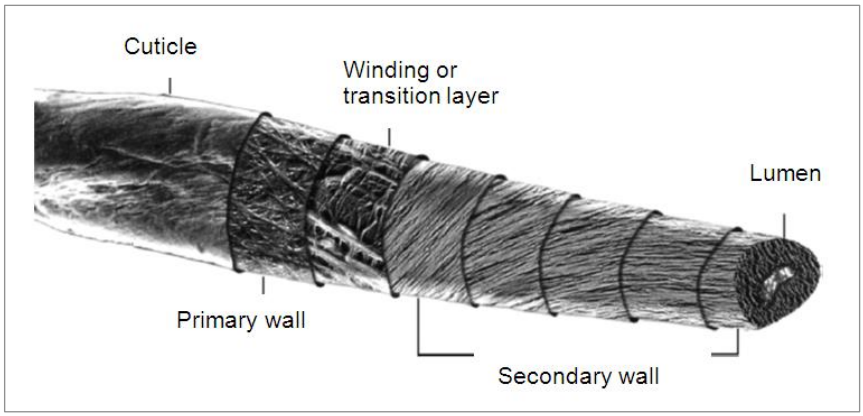

Figure 1.2.1 Structure of cotton (Wakelyn & Betroniere, 2007)

The cuticle exists as the separable outer boundary and consists of a layer of wax and pectin material. This layer plays an important role in providing lubrication to cotton during spinning operation in the textile industry. Below this layer is the primary wall, which consists primarily of a network of cellulose fibrils. Cellulose is the major component of cotton. Apart from cellulose, cotton is also associated with other external substances. In Table 1.2.1 the composition of typical mature cotton fiber is presented (Wakelyn & Betroniere, 2007; Krassig, 1985; Schick, 1975; Zeronian & Nevell, 1985; McCall & Jurgens, 1951).

Table 1.2.1 Composition of cotton fiber (McCall & Jurgens, 1951)

Constituent	**%**
Cellulose	94.0
Protein	1.3
Pectin	1.2
Wax	0.6
Ash	1.2
Other Substances	1.7

Inorganic cations as salts of organic acids or inorganic anions are one of the origins of impurities in composition of cotton and present in the lumen. The inorganic salts (phosphates, carbonates, and oxides) and salts of organic acids present in the raw fiber are reported as percent ash (about 1.2% of fiber dry weight). During the production of cotton, the plant absorbs potassium and other metals as normal nutrients from soil. Metals are incorporated from the soil into plants as natural constituents. In addition to metals absorbed by plant tissue, soil and plant parts may be deposited directly onto the lint, especially during harvesting. Ca, P, S, K, and Fe are elements of plant part and Mg, Al, Si, Fe, Cr, Se, Hg, Ni, Cu, K, and Ca are soil elements (Wakelyn & Betroniere, 2007). A quantitative summary of metal content in cotton is summarized in Table 1.2.2.

Table 1.2.2 Metal content of cotton (Wakelyn & Betroniere, 2007)

Metal	**ppm**
Potassium	2000-6500
Magnesium	400-1200
Calcium	400-1200
Sodium	100-300
Iron	30-90
Manganese	1-10
Copper	1-10
Zinc	1-10
Lead	not detected
Cadmium	not detected
Arsenic	trace (<1)

The secondary source of inorganic content of cotton fiber is the deposition of wind-borne particles onto the outer surface of the fiber. Although such particles may be present only in trace amounts, their presence in cotton has a significant effect on next processes, because they can make some difficulties in yarn manufacturing,

bleaching, and dyeing. Silicon as silica and other metals as oxides can cause frictional problems in rotor spinning and needle wear in knitting. Iron and copper metal particles, introduced to the fiber through deposition from machinery parts, can cause problems in the peroxide bleaching process as well as contribute to a permanent coloration that may affect dyeing. Peroxide bleaching also can be affected by magnesium salts. Insoluble calcium and magnesium salts can interfere with dyeing and copper and iron can contribute to yellowing of the finished denim goods. Iron can contribute to the permanent brown or pink color of the fiber, which influences on the final color of dyed fabric. Copper and zinc are metals of potential concern in wastewater effluents from textile dyeing and finishing. The levels of these metals in cotton fiber are low enough so that they do not contribute significantly to effluent problems. The metals are removed for the most part by proper scouring and bleaching processes that are used to prepare the fiber and fabric for dyeing and finishing (Wakelyn & Betroniere, 2007).

Although the primary wall accounts for only 5% of the weight of the fiber, it contains most of the non-cellulosic components found in the cotton. During bleaching the non-cellulosic components are removed and cotton is 99% cellulose. Cellulose a high molecular weight linear polymer composed of D-glucose building blocks, joined by β-1, 4-glucosidic bonds (Figure 1.2.2). In native cellulose as in cotton fibers, up to 10,000 β-anhydroglucose residues are linked to form a long chain molecule. The glucosidic linkages between the anhydroglucose units acts as a functional group and this, along with the hydroxyl groups, determine the chemical properties of cellulose. Each chain has two distinct ends, one called a non-reducing end and the other a reducing (potential aldehyde) chain end. Each anhydroglucose ring has three hydroxyl groups, and yet cellulose is not water soluble (Wakelyn &Betroniere, 2007; Krassig, 1985; Schick, 1975; Zeronian & Nevell, 1985; McCall & Jurgens, 1951).

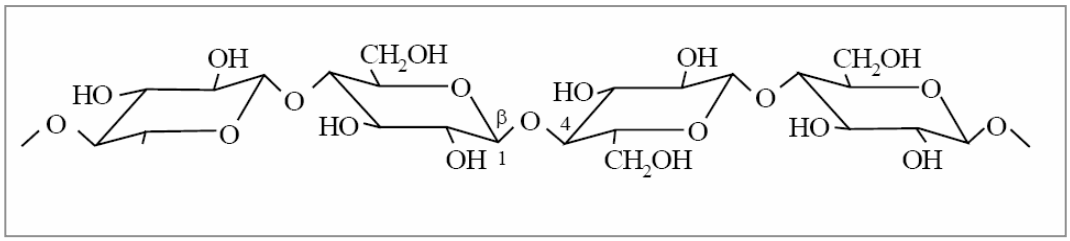

Figure 1.2.2 Structure of cellulose (Krassig, 1985)

1.2.2 Desizing of cotton

Most of the spun yarns and the main part of filament yarns have to be sized before weaving. Sizing is carried out in the weaving mill to protect the warp yarn during the weaving process from damage or break. The size forms a protective film on the warp yarn, protruding fiber ends causing loom stops are minimized (Schönbergr & Schäfer, 2003). About 75% of sizing agents used worldwide are starch and its derivatives (Cavaco- Paulo & Gübitz, 2003).

Desizing is a typical process in pretreatment of cotton woven fabrics and cotton blends but also necessary for all grey synthetic materials containing sizes. The sizing agents on the warp yarns, applied in weaving mills for better weaving efficiency, have to be removed before further processing in textile finishing (Cavaco- Paulo & Gübitz, 2003; Feitkenhauer et al. 2003; Schönbergr & Schäfer, 2003; Schao-Wei & Da-Nian, 2008; Hashem, 2007; Diderichsen, 1995). Desizing is performed as a first step in pretreatment or as a second step after singeing. Water-insoluble sizing agents have to be degraded during desizing, meanwhile water-soluble sizes can be simply washed out (Schönbergr & Schäfer, 2003). In the past, hydrogen peroxide and sodium hydroxide were generally used as desizing agents. But this method was not economically and environmental-friendly, due to high chemical oxygen demand (COD) and biological oxygen demand (BOD) in effluent, extreme pH, high concentrations of chemical used in process and high temperature (Buschle-Diller et al. 1998; Ibrahim et al. 2004).

1.2.3 Acid demineralization

Removing earth alkalis and cationic metal particles from cotton fabric is not possible by normal washing or treatment in alkali (Hebeish et al. 2001; Karmakar, 1999). Basically there are two ways to eliminate minerals and cationic metal cations: generating more soluble salts such as acid-demineralization and use of sequestering agents (Karmakar, 1999; Hvattum & Turner, 1951). Practically, a combination of acid- demineralization and sequestering agents is applied in textile industry in order to remove the metals effectively and uniformly. As a result catalytic damaging which is originated from peroxide bleaching will be minimized. Moreover, acid-demineralization can reduce the possible accumulation of hardly soluble earth alkalis (Hvattum & Turner, 1951). Even and more brilliant dyeing and also reduction in amount of peroxide used are the other benefits (Hvattum & Turner, 1951; Trotman, 1970).

1.2.4 Enzymatic processes of textiles

1.2.4.1 Structure and functions of enzymes

Since several years ago enzymes have been used in textile industry and a lot of efforts have been dedicated to replace the conventional chemical processes with corresponding enzymatic ones. The first use of enzymes in textile processing was reported in 1875, when starch–sized cloth was soaked with liquor containing barely. In 1900 this process was slightly improved using malt extract. But only the use of animal and bacterial amylases was the process of enzymatic desizing introduced into many textile factories. Interestingly, amylases remained the only enzymes applied in textile wet processing for almost 70 years (Cavaco- Paulo & Gübitz, 2003). Enzymes are high molecular weight proteins produced by living organisms to catalyze the chemical reactions that constitute metabolisms in living systems; they accelerate the rate of chemical reaction without themselves undergoing any permanent chemical change. As the enzymes are proteins, they consist of one or more polypeptide chains and display typical properties of proteins.

Protein is a complex 3-dimentional structure, which is composed of amino acids (Schindler & Hauser, 2004; Illanes, 2008). Figure 1.2.3 shows the structure of amino acid chains as building block of proteins and enzymes.

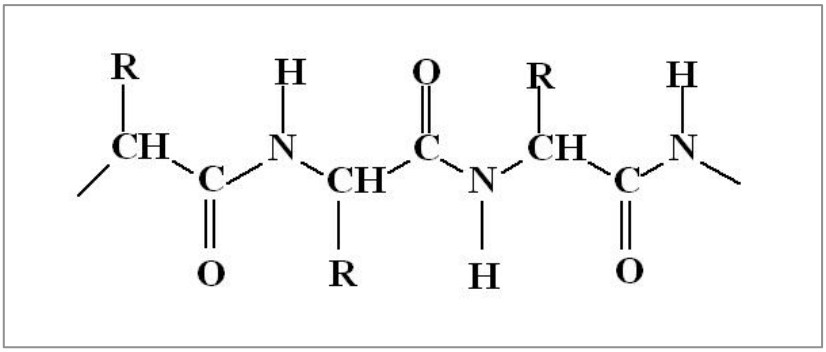

Figure 1.2.3 Structure of amino acids chain (Schindler & Hauser, 2004)

Enzymes differ from chemical catalysis in several important ways (Shuler & Kargi, 2002; Garratt & Grishham, 1999; Copeland, 2001; Walsh, 2002):

1. Enzyme-catalyzed reactions are at least several orders of magnitude faster than chemically-catalyzed reactions. Compared to the corresponding reactions enzymes typically enhance the rates by 10^6 to 10^{13} times.
2. Enzymes have more reaction specificity than chemically-catalyzed reactions and they rarely form byproducts.
3. Enzymes catalyze reactions under comparatively mild reaction conditions, such as temperatures below 100 °C, atmospheric pressure and pH around neutral. Conversely, high temperatures, high pressures and extremes pH are often necessary in conventional chemical catalysis.
4. Enzymes are biodegradable, usually safe and easy to control.

In textile finishing processes the application of enzymes is emerging and in some cases conventional chemical finishing processes are replaced by enzymatic finishing. In Table 1.2.3 the main enzymatic processes (yet available or in emerging state) are listed.

Table 1.2.3 Enzymatic processes in textile industry (Schindler & Hauser, 2004; Quand & Kühl, 2000; Parvinzadeh, 2009; Kiumarsi & Parvinzadeh, 2010; Klun et al. 2003; Silva & Cavaco-Paulo, 2004)

Type of Enzyme	**Textile Use and Effects**
Cellulases	Biopolishing of cotton and linen, biostoning, luster improvement and stone –washed effects on denim – hydrolyzing of cellulose
Amylases	Desizing of warp cotton yarn – hydrolyzing of starch
Proteases	Removing of protein-containing soils or stains from an textile article (in detergents), antifelting of wool, degumming of silk, modification of polyamide fibers to improve wettability and better coloration (in development) – hydrolyzing of protein
Lipases	Hydrolyzing of lipids from a textile article (in detergents), modification of polyamide fibers to improve wettability and better coloration (in development)
Pectinases	Bioscouring of cotton and hemp fibers – hydrolyzing of pectin
Catalases	Catalyzing the decomposition of hydrogen peroxide after bleaching process
Peroxidases	Used as an enzymatic rinse process after reactive dyeing, oxidative splitting of hydrolyzed reactive dyes on the fiber and in the liquor, providing better wet fastness, decolorized waste water and potentially toxic decomposition compounds
Ligninases	Removing of burrs and other undesired plant compounds from raw material – hydrolyzing of lignin
Collagenases	Removing the residual skin parts in wool – hydrolyzing peptide bonds in collagen
Esterases	Modification of polyester fibers to improve wettability (in development) – hydrolyzing of ester bonds
Nitrilases	Modification of acrylic fibers to improve wettability and better coloration (in development) – hydrolyzing of nitrile

An enzyme similar to a conventional catalyst accelerates a chemical reaction progress via the formation of an unstable intermediate between reactants and products in the transition state. If the energy available in the system as collision energy is higher than a certain potential barrier, the reaction will take place. A catalyst (in this case: enzyme) accelerates a chemical reaction without any changes in its extent and with no overall thermodynamic effect, i.e. the level of free energy change is the same in presence or absence of the catalyst (Figure 1.2.4). Thus, the enzyme reduces only the amount of activation free energy to overcome the potential barrier, which leads to more stable transition intermediate (Shuler & Kargi, 2002; Garratt & Grishham, 1999; Copeland, 2001; Walsh, 2002; Lancaster, 2002).

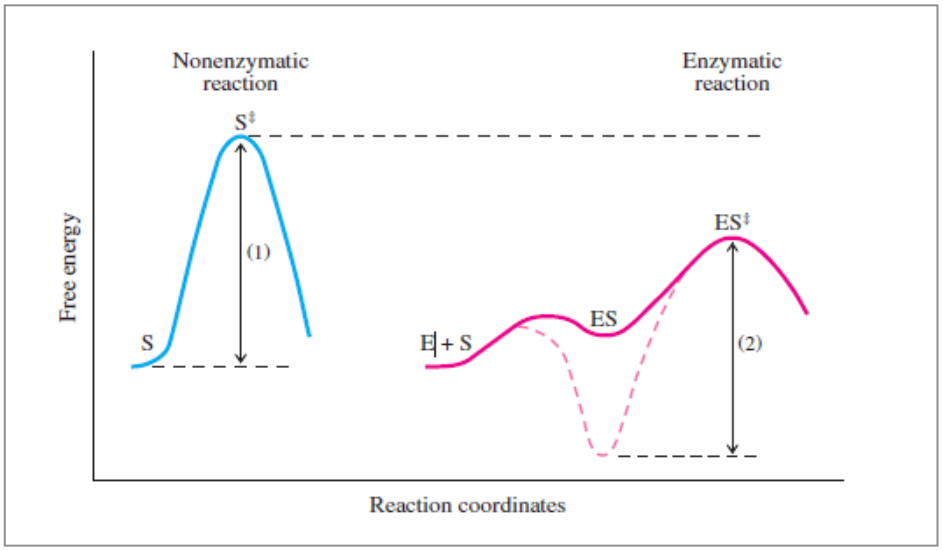

Figure 1.2.4 Change in free energy in catalyzed and non-catalyzed reactions

(Robert Horton et al. 2006)

1.2.4.2 Enzymatic decomposition of hydrogen peroxide

Hydrogen peroxide is one of the most used chemicals in conventional bleaching of cotton articles. Decomposition of hydrogen peroxide is a necessary process which reduces the water consumption during washing of the bleached cotton and prevents problems in further dyeing (Rouette, 2001). Catalases were successfully introduced to the textile industry for the removal of hydrogen peroxide after

bleaching and prior to dyeing. Catalases convert hydrogen peroxide into water and oxygen showing first order kinetics. This loop reaction starts by oxidation of the catalase to compound I by one molecule of hydrogen peroxide yielding water and regeneration via production of oxygen from the second molecule of H_2O_2 (see reactions (1.1) and (1.2)). Usually catalases have heme-containing prosthetic groups. Bifunctional catalase-peroxidases can oxidize substrates other than H_2O_2. In the first step catalase-peroxidase compound I is formed because of oxidation by peroxide. Compound I is situated two oxidation equivalents higher and has a porphyrin-p-cation radical with an iron (IV) center and can be reduced to the starting form by hydrogen peroxide. Alternatively compound I can be reduced by a one-electron reduction to Compound II, which is the peroxidase reaction. Compound II has an amino acid radical ($R^{\bullet}$) and iron (III). Finally, Compound II is reduced to the starting form by a second one-electron reduction (Costa et al. 2001; Gudelj et al. 2001; Zamocky et al. 2001):

$$\text{Fe (III) ... R} + H_2O_2 \rightarrow [\text{Fe (IV) = O ... R}]^{\bullet +} + H_2O \quad (1.1)$$

Ferric enzyme — Compound I

$$[\text{Fe (IV) = O ... R}]^{\bullet +} + H_2O_2 \rightarrow \text{Fe (III) ... R} + O_2 + H_2O \quad (1.2)$$

Compound I — Ferric enzyme

$$[\text{Fe (IV) = O...R}]^{\bullet +} + AH_2 \rightarrow [\text{Fe (III) = O...R}]^{\bullet +} + AH^{\bullet} \quad (1.3)$$

Compound I — Compound II

$$[\text{Fe (III) = O...R}]^{\bullet +} + AH_2 \rightarrow \text{Fe (III) ... R} + AH^{\bullet} \quad (1.4)$$

Compound II — Ferric enzyme

Catalases catalyze reactions (1.1) and (1.2) and catalase-peroxidases catalyze reactions (1.1), (1.3) and (1.4). During lignin degradation, fungi employ so-called manganeseperoxidases (EC 1.11.1.13) requiring the presence of manganese ions:

$$2Mn\ (II) + 2H^{+} + H_2O_2 \rightarrow 2Mn\ (III) + 2H_2O \qquad (1.5)$$

These enzymes and other peroxidases can also be used for textiles dye degradation. Catalases and peroxidases activities can be measured spectrophotometrically following the degradation of hydrogen peroxide at 240 nm and the color change during the oxidation of various substrates, respectively (Costa et al. 2001; Gudelj et al. 2001; Zamocky et al. 2001).

1.2.4.3 Biofinishing of cellulosic fibers by cellulases

Cellulases are the most successful enzymes used in processing of textiles (Cavaco-Paulo & Gübitz, 2003). They are mainly applied for biostoning of jeans, finishing of cotton and cotton blended fabrics to obtain improved softness and remove of fuzz and pills. The most likely mechanism of enzymatic depilling/cleaning is the action of the enzyme (adsorption/hydrolysis) on easily accessible pills (or fibrils) at the surface of a fabric (Durán & Duráa´n, 2000; Csiszár et al. 1998; Tyndall, 1990; Koo et al. 1994; Chikkodi et al. 1995; Tyndall, 1992). Cellulase is a multicomponent mixture of cellulose-degrading enzymes (Klyosov, 1990). There are at least three major groups of cellulase involved in the hydrolysis of cellulose: endogluconase, exogluconase or cellobiohydrolase and β-glucosidase. They act simultaneously or in synergism (Csiszár et al. 1998; Tyndall, 1990; Koo et al. 1994; Chikkodi et al. 1995; Tyndall, 1992; Klyosov, 1990; Philippidis, 1994). It has been suggested that endogluconases (EGs) randomly cleave cellulose into smaller fragments generating new ends which are also thought to erode crystalline regions of cellulose making them more susceptible to EG attack (Wood, 1992). Cellobiohydrolases or exoglucanases are necessary for complete hydrolysis of crystalline region. They attack at crystalline ends of the cellulose strands. This action produces dimer units

referred to as cellobiose. Cellobiases are cellulases that attack the cellobiose to yield two glucose units. The enzyme acts as a catalyst to break down complex carbohydrates, cellulose, into simple carbohydrates, glucose (Rousselle et al. 2002; Stewart, 2005). Figure 1.2.5 illustrates the mechanism of hydrolysis of the band in cellulose to yield glucose and cellobiose.

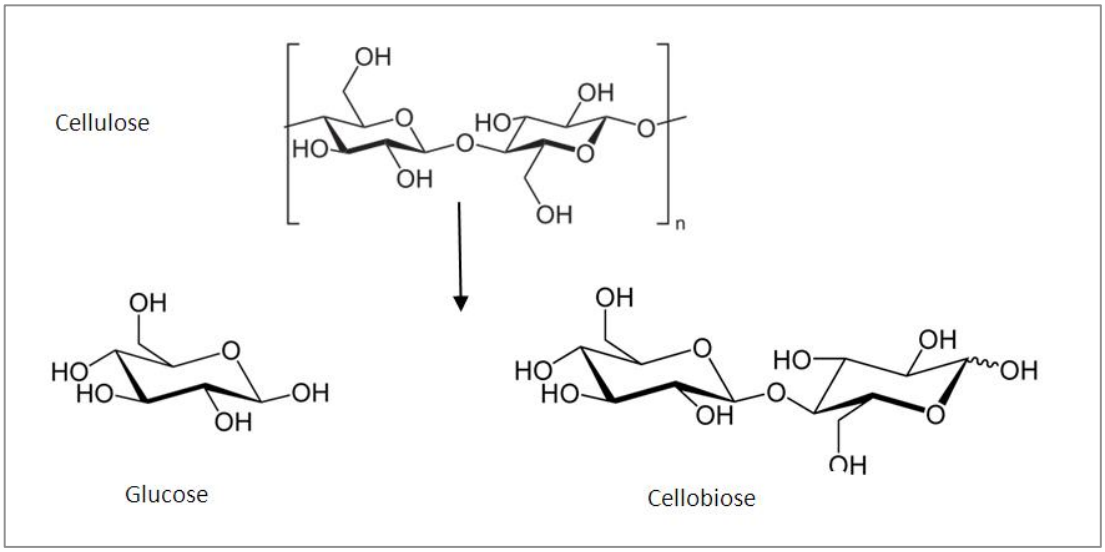

Figure 1.2.5 Hydrolysis of cellulose into cellobiose and glucose

1.2.4.4 Enzymatic scouring of cellulosic fibers

Waxy materials and pectin are responsible for the hydrophilic properties of raw cotton. Therefore, removal of waxy materials and pectin components from the cotton cell wall by scouring is claimed to improve fiber hydrophilicity and facilitate dye penetration (Batra, 1985; Etters et al. 1995). Conventional scouring process has been performed in alkaline medium at boiling temperature. This process needs large quantities of chemicals, energy and water and also decreases the tensile strength of fabric (Tzanov et al. 2001). Thus, it has been tried to replace the conventional alkaline boiling scouring with enzymatic process. Different individual enzymes and their mixtures were studied: pectinases, cellulases, proteases and lipases (Hsieh et al. 1996; Yonghua & Hardin, 1997; Robner, 1993). Pectinase, as a

pectin-degrading enzyme, seems to be the most suitable enzyme for this purpose. Pectinase is able to break the pectin into low molecular water soluble oligomers without causing cellulose destruction (Tzanov et al. 2001).

1.2.4.5 Enzymatic bleaching of cellulosic fibers

Bleaching is conventionally performed by using of hydrogen peroxide under boiling conditions and alkaline medium to remove natural colorants. Despite high efficiency of peroxide-bleaching, large amount of rinse water and highly chemical consumption are the disadvantageous of this process. Furthermore, hydrogen peroxide can cause fiber damage through radical reactions, especially in presence of metal ions. Major alternative for nontoxic and environmental-friendly bleaching is enzymatic process based on peroxidases, laccase/mediator systems and glucose oxidases. These enzymes have quite different mechanisms (Buschle-Diller et al. 2001). Among other catalytic functions, peroxidases can promote the reaction of oxidizing agents such as hydrogen peroxide (Colonna et al. 1999). Laccases are a group of enzymes that are able to catalyze the breakdown of the chromophore in colored components. Due to their nonspecific mode of action, organic mediator components are usually essential. The mediators direct the transfer of electrons between the active site of the enzyme and the substrate. Laccases together with manganese peroxidases have been used for processing lignin-containing fibers such as kenaf and flax. Laccases have also been applied for bleaching indigo in denim fabrics (Cavaco-Paulo, 1999; De, 1998).

Glucose oxidase has been employed in the bleaching process based on controlled production of hydrogen peroxide during oxidation of glucose released meanwhile of enzymatic desizing. The enzyme is highly specific for β-D-glucose. The resulting gluconic acid has been reported to serve as a sequestering agent of metal ions (Cavaco- Paulo & Gübitz, 2003; Buschle-Diller et al. 1998).

1.2.4.6 Enzymatic finishing of protein fibers

The main protein fibers are wool and silk. Wool must be pretreated through various stages of processing and cleaning to remove dirt, grease, vegetable matters, and the other impurities. Most of the wet pretreatment processes of wool are carried out under very mild agitation owing to the tendency of wool to felt. The felting problem in wool fibers originates from presence of 'scales' in the cuticle on the wool surface. Wool has to be modified by oxidation or addition of polymers as antishrinkage pretreatment to remove the scales. Most of chemicals used for this process are environmentally harmful. Enzymatic treatment as the alternative has been developed (Cavaco- Paulo & Gübitz, 2003; Das & Ramaswamy, 2006).

The effectiveness of proteolytic and lipolytic enzymes has been studied to improve wool properties such as shrink resistance, softness and wettability. The protein disulphide isomerase improves the shrinkage behavior of wool fabrics. Transglutamnase can enhance shrinkproofing of wool via formation of new crosslinks and liberation of ammonia. Attempts to replace carbonization of wool by enzymatic treatments have been made using a range of different enzymes to remove vegetable matter, reducing the amount of necessary sulfuric acid used (Jovancic et al . 1998; Bishop et al. 1998; Chikkodi et al. 1995; Nolte & Bishop, 1996; Cavaco-Paulo, 1998). Laccases, peroxidases and haloperoxidases have also been proposed for use as antishrink treatments of wool. Oxidative enzymes are believed not to degrade wool fibers but able to modify the chemistry of amino acid residues (Lantto et al. 2004).

Silk is composed mainly of sericin (22-25%), fibroin (62.5-67%), water and mineral parts. Sericin and fibroin are proteins. The main part of silk is fibroin, which is insoluble in water and sericin acts as a gum binder and is more water-soluble than fibroin. This sericin must be removed from the silk by degumming process, because sericin makes a harsh and stiff feeling in fiber and reduces the luster and whiteness of silk. Also it prevents the penetration of dye and other solutions during wet process. In degumming sericin is hydrolyzed and the amide bonds of the long

protein molecules are broken into smaller fractions which dispersed and solubilized. But conventional degumming processes (extraction with water at 115 °C, boiling off in soap or with alkalis and using of boiling acidic solutions) cause a 20-25% weight loss and also environmental pollutions. Enzymatic degumming overcomes these defects, through specific hydrolyzing of peptide bonds in sericin. Some enzymes such as proteases and lipases have been used to hydrolyze sericin in mild conditions. The application of savinases, alcalases and their mixtures has been reported (Arami et al. 2007).

1.2.4.7 Enzymatic treatment of synthetic fibers

Enzymatic modification of synthetic fibers is a new area in application of biotechnology in the textile industry. The main goal of enzymatic treatment is modification and improvement of some physical and chemical properties, mainly: wettability, dye adsorption and etc. The most researches of enzymatic treatment of synthetic fibers belonged to acrylic fibers. In the case of polyester and polyamide just a few studies have been carried out. It was found that nitrile groups of polyacrylonitrile fibers (PAN) can be converted to the corresponding acid or amino acids by nitrilases or by an enzyme system consisting of nitrile hydratase and amidase, respectively and sensible increase in hydrophilicity is obtainable. It has been shown that the high crystallinity of certain PAN materials have a negative influence on susceptibility to enzymatic hydrolysis. Enzymes that can hydrolyze plolyamides are proteases, amidases, amidases, cutinases, and lipases. Polyester fibers can be also hydrolyzed by cutinases, lipases, and esterases (Parvinzadeh, 2009; Kiumarsi & Parvinzadeh, 2010; Klun et al. 2003; Silva & Cavaco-Paulo, 2004; Gübitz & Cavaco-Paulo, 2007; Gübitz & Cavaco-Paulo, 2003; Siva et al., 2005; Tauber et al. 2000; Battistel et al. 2001; Bucheńska, 1997; Matamá et al. 2007; Kobayashi & Shimizu, 1994; Singh et al. 2006; Donelli et al. 2009).

1.2.4.8 Enzymatic desizing of cotton

As it described in 1.2.2 the main sizing agent for cotton is starch and its derivatives. Starch is a polymer substance consisting glucose units linked to one another

through the C1 oxygen known as glycosidic bonds. The stability of glycosidic bond depends on pH: at higher pH this bond is more stable and at lower pH can be hydrolyzed. The aldehyde group at the end of polymeric chain is a reducing end. Starch contains two types of glucose polymers (or alphaglucan): amylose and amylopectin. Amylose and amylopectin represent about 98-99% of the dry weight of starch. These polysaccharides varied according to the origin of the starch. Structure and properties of amylose and amylopectin are different. Amylose is a relatively long and linear alpha-glucan polymer consisting up to 6000 glucose units, with α 1-4 glucosidic bonds (Figure 1.2.6). Amylopectin is a larger molecule than amylose with short α 1-4 linked linear chains of 10-60 glucose units and α 1-6 linked side chains with 15-45 glucose units (Figure 1.2.7). The typical degree of polymerization (DP) in amylopectin is 9600-15900. The average number of branching points in amylopectin is 5%. Amylose is water-soluble due to its low molecular weight, whereas amylopectin is not soluble in water and therefore removing amylopectin from sized cotton would be difficult (Tester et al. 2004; Buleon et al. 1998).

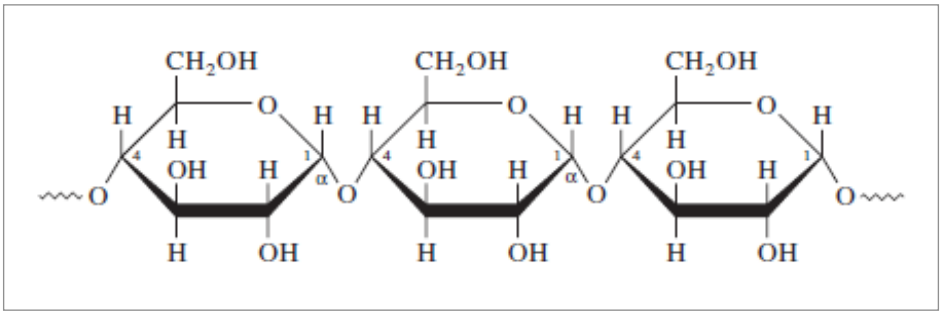

Figure 1.2.6 Chemical structure of amylose (Horton et al. 2006)

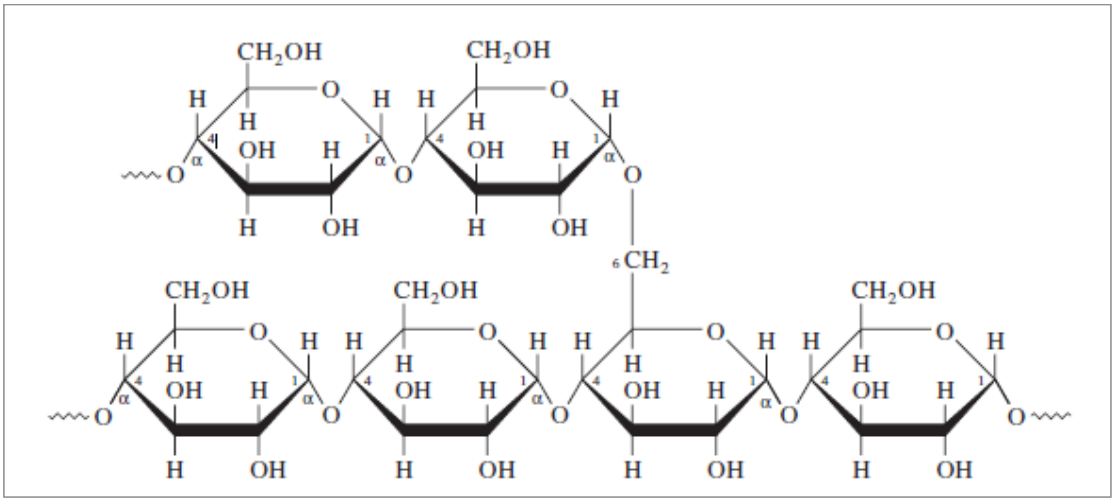

Figure 1.2.8 Chemical structure of amylopectin (Horton et al. 2006)

In conventional method of starch removing from a cotton article large amount of water, chemicals and energy have to be consumed. To decrease water and the chemicals consumption and in response to the environmental concerns, enzymatic desizing of cotton seems a practical alternative. There are four different groups of starch-converting enzymes: endoamylases, exoamylases, debranching enzymes and transferases (Figure 1.2.8). Endoenzymes can break α, 1-4 glycosidic bonds in the inner parts (endo-) of the amylose or amylopectin chains. α-amylase (EC 3.2.1.1) is a famous endoamylase. The final products of α-amylase action on starch are oligosaccharides with different chain length. The second group of starch-converting enzymes is exoamylase, which either cleaves just α, 1-4 glycosidic bonds such as β-amylase (EC 3.2.1.2), or act on both α, 1-4 and α, 1-6 glycosidic bonds, like amyloglucosidase or glucoamylase (EC 3.2.1.3) and α-glucosidase (EC 3.2.1.20). The external glucose residues of amylose or amylopectin are the substrates of exoamylases. Therefore, the product of this reaction is exclusively glucose (glucoamylase and α-glucosidase) or maltose and β-dextrin. It should be noted that the substrate preference in the action of glucoamylase and α-glucosidase is different: α-glucosidase has a better performance in hydrolyzing of short maltooligosaccharides. In this reaction glucose with α-configuration is liberated, while glucoamylase acts on long chain polysaccharides (Van der Maarl et al. 2002).

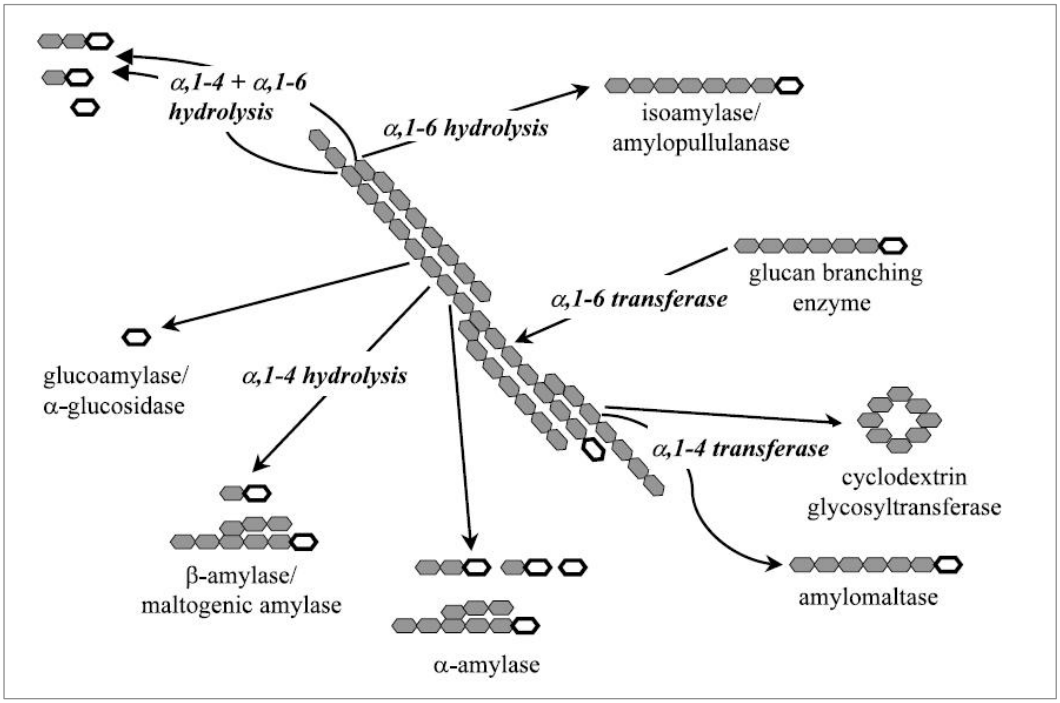

Figure 1.2.9 Action of different enzymes on hydrolyzing of starch (Van der Maarl et al. 2002)

Debranching enzymes are the third group of starch-converting enzymes with ability of hydrolyzing α, 1-6 glycosidic bonds. Isoamylases (EC 3.2.1.41) and pullanases type I (EC 3.2.1.41) belong to this group. The main difference of pullalanase and isoamylase is hydrolyzing of pullalan, which is a polysaccharide with a repeating unit of maltotriose linked by α, 1-6 glycosidic bonds. Isoamylase can only hydrolyze α, 1-6 glycosidic bonds in amylopectin, while pullalanase can hydrolyze the same bonds in pullalan and amylopectin. The other types of pullalanse enzymes hydrolyze both α, 1-4 and α, 1-6 glycosidic bonds, belong to group II pullalanase and referred to as α-amylase-pullalanase or amylopullalanase. The major products of this reaction are maltose and maltotriose (Van der Maarl et al. 2002; Kelkar & Deshpande, 1993).

Transferases are the fourth group of starch-converting enzymes that can hydrolyze α, 1-4 glycosidic bonds of the donor molecule and transfer part of the donor to glycosidic acceptor with the formation of a new glycosidic bond. Amylomaltase (EC 2.4.1.25) and cyclodextrin glycosyltransferase (EC 2.4.1.19) form a new bond, while

branching enzyme (EC 2.4.1.18) forms a new α, 1-6 gylosidic bonding (Van der Maarl et al. 2002).

1.3 Aims of study

This part focuses on new ways of the cotton pretreatment with help of enzyme technology. The aim of study is to investigate the possibility of acid-demineralization of cotton woven fabric without any extra process. To achieve this goal, a practical way could be the integration of acid-demineralization with enzymatic desizing. Enzymatic desizing with the conventional starch-converting enzymes is carried out at neutral pH values. On the other side, acid demineralization must be done in acidic conditions. Using novel industrial acid stable α-amylases and glucoamylases provides enzymatic desizing in acidic condition. Thus, acid-demineralization can be simultaneously carried out.

1.4 Basic approaches

Shortening and simplification of pretreatment processes in textile industry through combination of two or more stages is one of the main trends of development in this field. The important processes, such as desizing, scouring and bleaching are usually carried out in separate stages in conventional processes. Also consumption of large amount of energy and water is the other aspect of conventional preparation. It has been already known that, to minimize the energy and water consumption the combination of several stages of pretreatment processes by lowering the number of operations or reducing the time of reaction is absolutely necessary. In this regards, all efforts have been directed to combination of pretreatment processes and also development of some continuous and semi-continuous machineries, including process integration to enable combined desizing/scouring, scouring/bleaching or desizing/scouring/bleaching. Among the integrated pretreatment processes a number of low temperature processes have also been developed, such as batch scouring and bleaching in temperature range of 25-45 °C. In all the mentioned accelerated processes, cost saving in steam, water, and electricity with little increase in chemical costs is obtained (Karmakar 1999).

On the other hand, there is a greet tendency to use enzymes in chemical processes and also in chemical pretreatments of textiles. This trend is originated from the massive benefits of enzymes in lowering the use of chemicals and possibility of executing more environmental friendly industrial processes. Enzymes show the most activity in the neutral pH values and in the mild reaction conditions, such as temperatures below 100 °C. α-amylase and glucoamylase behave the same rule. Bacillus licheniformis α-amylase (BLA) is probably the most extensively thermostable natural enzyme for converting of starch (Heng et al. 2005). However, the use of α-amylase has been limited due to its instability in the pH values below 6. Demand for designing and producing acid-stable starch-converting enzymes such as α-amylase and glucoamylase began from food industry. Since native corn starch has a natural pH 3.2–3.6, this brings about heavy costs of raw material and process operating for pH adjusting at a large scale. Thus, design and develop of enzymes

operating at lower pH was a demand (Heng et al. 2005). Since some years ago, the acid-stable starch-converting enzymes have been produced in industrial scales to meet the needs of industry.

In response to the demands of different industries, especially food industry, some efforts have been dedicated to develop some more stable starch-converting enzymes, which can be used under the mild acidic conditions. This development in industrial starch-converting enzymes (i.e. α-amylases and glucoamylases) can provide the possibility of combination of acid-demineralization and enzymatic desizing. Therefore, the combination of acid-demineralization with enzymatic desizing, which is carried out at pH-range of 2–3 by use of acid stable glucoamylases and α-amylases seems to be a practical way to remove the cationic metals simultaneously with desizing.

In this study the possibility of simultaneous acid-demineralization and enzymatic desizing of cotton fabric at low pH has been investigated using commercially available glucoamylases and α-amylases and also their mixture, which are relatively active at low pH. The performance of enzymatic desizing was evaluated by measuring the remaining starch, absorbency of the treated cotton fabric, and loss in fabric weight after desizing. Acid-demineralization was simultaneously carried out by pH adjusting (pH 2) of desizing solution. Also the concentrations of cationic metals (namely: calcium, potassium, manganese, magnesium, sodium, copper, iron, and zinc) were measured after completion of the process.

1.5 Experimental

1.5.1 Materials

1.5.1.1 Enzymes

α-amylases Optisize Next, Optisize HT Plus, Optisize 160, Optisize HT 520 (bacterial, activity 13400-14600 AAU/g, EC 3.2.1.1) and glucoamylase Multifect GA 10L (fungal, activity 12500-13500 AAU/g, EC 3.2.1.3) were purchased from Genencor, Rochester NY/USA and used without any further purification.

1.5.1.2 Cotton fabric

An industrial plain woven cotton fabric (density120.66 g/m^2) was supplied by Textilveredlung an der Wiese GmbH, Lörrach/Germany. The warp yarns of fabric were sized just with potato starch.

1.5.1.3 Buffer solutions and other chemicals

To protect the activity of enzymes in a specific pH enzymes should usually be used in a buffer solution (Cavaco- Paulo & Gübitz, 2003). The enzymatic desizing was done in different pH values: pH 2 and pH 5. For pH 5, the buffer was prepared by acetic acid (6.1 ml/l–Fluka) and sodium acetate (8.2 g/l–Fluka). To prepare a buffer solution for pH 2, 6.8 ml/l of phosphoric acid 85% (Fluka) and 12.8 g/l of monopotassium phosphate (Fluka) were used. Beixon NE as chelating agent and Felosan NKB as nonionic surfactant were kindly supplied by CHT R. Beitlich GmbH, Tübingen/Germany. Potassium iodine, iodine and methanol to prepare iodine-solution were purchased from Merck, sodium acetate and nitric acid (65%) were products of Fluka.

1.5.2 Methods

1.5.2.1 Enzymatic desizing of cotton fabric

Enzymatic desizing of cotton was carried out under different conditions: desizing at pH 2 and desizing at pH 5. Desizing at pH 5 is a conventional enzymatic desizing process and desizing at pH 2 is a desizing process under acidic conditions. The aim of desizing at pH 5 was comparison of desizing effectiveness under acidic condition and desizing under normal condition. Every desizing solution contained enzymes (8 ml/l and 16 ml/l for each one of enzymes), Beixon NE (8ml/l) and Felosan NKB (4 ml/l). The liquor-to-goods-ratio was 1:25 and the weight of fabrics was approximately 1.0 g. The same solutions without enzymes were used as blank tests. Also, to investigate the effectiveness of chelating agent, solutions with similar ingredients but in absence of the chelating agents were employed. Every desizing process was done at different temperatures: room temperature and 60 °C for 60 min and overnight. Finally the samples were rinsed with tap water and distilled water, dried at room temperature and conditioned (20 °C, 65 % humidity, 24 h).

1.5.2.2 Evaluation of desizing performance

The performance of desizing was evaluated by measuring the drop penetration test, starch detection and weight loss of fabric (gravimetric test). Drop penetration test and starch detection were performed according to TEGEWA method.

Drop penetration time was measured by employing of an aqueous dye solution based on TEGEWA provision. In this test, a drop of defined volume (0.05 ml of a 2 % solution of the dye Amido Blue V-PW) from a height of 40 mm dropped on the sample and found the time to complete the sinking as penetration time (Arbeitsgruppe "Textilvorbehandlung", 1987).

To evaluate desizing degree, the samples were stained with an iodine-solution and starch content was determined by comparison with a standard color scale, according to TEGEWA provision. Consequently the amount of starch in cotton as a

function of the appeared blue color rated from 1 to 9. The grade 1 characterized a fabric with high level of starch (not desized). With increasing grade the quality of desizing would be better. With a grade 6 or more the goods are effectively desized (Arbeitsgruppe Textilvorbehandlung, 1981).

The weight difference of samples before and after desizing corresponds to weight loss and more weight loss means better desizing. The weight difference was calculated as decreased weight of the conditioned samples before and after desizing with the starch-converting enzymes, according to the following equation:

$$\text{Relative weight decrease (\%)} = \frac{m_1 - m_2}{m_2} \times 100$$

Equation 1 Relative weight decrease

Where m_1 is the weight of original sample and m_2 is the weight of sample after enzymatic desizing.

1.5.2.3 Measurement of the cationic metals

The concentrations (ppm) of calcium, potassium, manganese, magnesium, sodium, copper, iron and zinc were measured. To analyze the remaining metals quantitatively, approximately 0.2 g of the samples were digested with 8.0 ml concentrate acid nitric (65%) in a microwave digester (MarsXpress, CEM, Kamp-Lintfort) at 180°C. After complete digestion of samples, the residual clear solutions were transferred to 100 ml volumetric flasks and filled with deionized water to dilute the solutions. Afterward the diluted samples were evaluated by using an inductively coupled plasma optical emission spectrometer (ICP/OES, Varian 720-ES, Kamp-Lintfort) to calculate the metal concentrations.

ICP/PES is one of the most effective and common analytical tools for detection and measurement of trace elements in variety of sample matrices. The technique is based on the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge. Sample pretreatment for solid

samples is different with liquid and gas samples. Solid samples should be extracted or require acid digestion, so that the analytes will be present in a solution, while liquid and gas samples may be injected directly into the instrument. ICP/PES is composed two parts: the ICP and optical spectrometer. The ICP consists of 3 quartz glass tubes and RF generator surrounds the quartz tubes. Argon gas is normally used for creation of the plasma. The sample solution is converted to an aerosol and directed into the central channel of plasma. The atoms and ions contained in the plasma vapor are excited into a state of radiated light (photon) emission. The radiation will be passed to the spectrometer, where it is dispersed into spectral components. By concerning the specific wavelengths emitted by each element, the most suitable line for the application is measured by means of charge coupled device (Meyers, 2011).

1.6 Results and discussion

1.6.1 Evaluation of enzymatic desizing

The possibility of enzymatic desizing in low pH values, especially pH 2 has been investigated. To achieve an effective acid-demineralization the desizing solution should be enough acidic. Thus, pH 2 was selected as the optimal pH for acid-demineralization. On the other hand, pH 5 was selected as the optimal pH for the best effective enzymatic desizing and comparison the results of desizing at pH 2, as the unconventional conditions of the enzymatic desizing. The other goal of these experiments was to select the most suitable enzymes for desizing at pH 2. Genencor has produced some special starch-converting enzymes, which are active in lower pH values, e.g. pH 3-4. These acid stable enzymes are: the α-amylases Optisize Next, Optisize HT Plus, Optisize 160, Optisize HT 520 (bacterial, activity 13400-14600 AAU/g, EC 3.2.1.1), and glucoamylase Multifect GA 10L (fungal, activity 12500-13500 AAU/g, EC 3.2.1.3). It was important to find the best process conditions (process time, temperature, concentration of enzymes) and also the most suitable enzyme or a mixture of enzymes with optimum efficiency under acidic conditions. Hence, for every enzyme two different concentrations (8ml/l and 16ml/l) were used at room temperature and 60 ^{o}C. The desizing at room temperature was carried out for 60 min and also overnight and the desizing at 60 ^{o}C was done just for 60 min. Furthermore, a combination of each α-amylase with the glucoamylase enzyme was employed. This combination was used due to the synergistic effect of glucoamylase and α-amylase.

The results of enzymatic desizing at pH 2 and pH 5 are presented in Tables 1.6.1 and 1.6.2. Three factors were used to analyze the effectiveness of desizing. These factors are: absorbency and starch detection (according to TEGEWA method) and gravimetric test.

Table 1.6.1 The results of enzymatic desizing at pH 2

Enzyme	Concentration	Starch Detection (TEGEWA)			Drop Test (mm:ss)			Weight Loss (%)		
		Room Temperature		60 °C	Room Temperature		60 °C	Room Temperature		60 °C
		60 min	Over Night	60 min	60 min	Over Night	60 min	60 min	Over Night	60 min
Optisize Next	8ml/l	3-4	4-5	2-3	02:27	01:39	03:05	7.04	7.34	4.36
	16ml/l	4	5	3	02:01	01:22	02:23	7.67	7.52	5.22
Optisize HT 520	8ml/l	2-3	3	3	04:21	03:18	07:23	5.63	6.34	3.91
	16ml/l	3	3-4	3-4	03:32	03:02	6:48	6.21	6.75	4.12
Optisize HT Plus	8ml/l	2-3	3	3	06:11	05:42	08:34	4.11	6.47	4.67
	16ml/l	2-3	4	3-4	05:43	05:23	07:22	5.33	6.82	5.06
Optisize 160	8ml/l	2-3	3-4	2-3	08:37	07:32	12:02	4.03	5.07	3.82
	16ml/l	3	3-4	3	07:25	06:50	10:34	4.15	5.23	4.07
Glucoamylase Multifect GA 10L	8ml/l	3	3-4	4	03:42	03:09	05:36	6.48	6.52	5.34
	16ml/l	3-4	4	4-5	03:05	03:12	04:32	6.92	7.05	6.12
Glucoamylase 10L+Optisize Next	8ml/l	4-5	6-7	5	00:21	00:10	01:06	8.16	9.18	7.34
	16ml/l	5	6-7	5-6	00:17	00:09	00:58	8.22	9.34	8.09
Glucoamylase 10L+Optisize HT 520	8ml/l	4	6	5	00:48	00:39	02:37	7.34	8.21	6.05
	16ml/l	4-5	6-7	5-6	00:41	00:30	01:48	7.45	8.26	6.39
Glucoamylase 10L+Optisize HT Plus	8ml/l	4	5-6	4	00:46	00:42	03:05	7.02	7.56	6.23
	16ml/l	4-5	6	4-5	00:39	00:38	02:25	7.33	7.80	6.67
Glucoamylase 10L+Optisize 160	8ml/l	3-4	4	3	01:06	00:56	04:34	6.53	6.86	5.12
	16ml/l	4	4	3-4	00:48	00:47	03:15	6.77	7.34	5.40
Blank	0	1	1	1-2	09:37	09:14	08:22	3.22	3.51	3.13

Table 1.6.2 The results of enzymatic desizing at pH 5

Enzyme	Concentration	Starch Detection (TEGEWA)			Drop Test (mm:ss)			Weight Loss (%)		
		Room Temperature		60 °C	Room Temperature		60 °C	Room Temperature		60 °C
		60 min	Over Night	60 min	60 min	Over Night	60 min	60 min	Over Night	60 min
Optisize Next	8ml/l	6-7	7	8	00:07	00:03	00:05	9.32	10.05	11.01
	16ml/l	8	8-9	8-9	00:06	00:02	00:02	9.46	10.77	11.09
Optisize HT 520	8ml/l	6-7	6-7	7	00:14	00:07	00:11	8.12	9.23	9.56
	16ml/l	7	8-9	7-8	00:11	00:05	00:06	8.37	9.46	10.22
Optisize HT Plus	8ml/l	6	6-7	7	00:23	00:17	00:08	8.16	8.41	10.23
	16ml/l	6-7	7	7-8	00:16	00:11	00:03	8.40	8.87	11.09
Optisize 160	8ml/l	6-7	7	6-7	00:46	00:33	00:42	7.21	8.09	7.53
	16ml/l	7	7	7	00:38	00:24	00:12	7.55	9.02	8.22
Glucoamylase Multifect GA 10L	8ml/l	6	7	7	00:06	00:02	00:03	8.77	10.23	10.41
	16ml/l	7	7	7-8	00:04	00:01	00:01	8.92	10.44	10.88
Glucoamylase 10L+Optisize Next	8ml/l	7	8	8	00:05	00:02	00:02	10.18	11.22	11.34
	16ml/l	7	8-9	9	00:02	00:01	00:01	10.66	11.78	11.78
Glucoamylase 10L+Optisize HT 520	8ml/l	6	6-7	7	00:20	00:11	00:09	7.21	7.23	8.12
	16ml/l	6-7	7	7-8	00:14	00:07	00:05	7.44	7.32	8.23
Glucoamylase 10L+Optisize HT Plus	8ml/l	7	7	7	00:19	00:12	00:08	7.46	7.67	9.13
	16ml/l	7	7-8	7	00:08	00:06	00:04	7.59	7.80	9.34
Glucoamylase 10L+Optisize 160	8ml/l	6	6-7	7	00:18	00:13	00:09	7.67	8.03	8.44
	16ml/l	7	7	7-8	00:15	00:09	00:06	8.23	8.56	8.67
Blank	0	1	1	1	10:11	09:45	09:30	3.69	3.8	3.92

To find the best conditions and the best enzymes or a mixture of enzymes the results of enzymatic desizing at pH 2 was compared with blank samples and also with the results of enzymatic desizing at pH 5. The important factors in effectiveness of desizing are temperature, time, concentration, and the suitable enzyme(s). In both tables, blank samples are the samples which were treated in the corresponding buffer solution in absence of enzymes.

The results of blank samples in both pH values are almost the same. It has been found that using a buffer solution without enzymes, even under acidic condition and high temperature (60 ^{o}C) cannot remove the potato size from the cotton fabric. There was a little difference between the results of desizing performance at pH 2. It is due to the effect of acidic condition which slightly improved the indicators, i.e. starch detection indicator from 1 in pH 5 to 1-2 at pH 2, drop test from 10:11 at pH 5 to 8:22 at pH 2 and finally weight loss from 3.92 to 3.13%.

Table 1.6.1 indicated that amongst the all enzymes used Optisize Next and specially its mixture with Glucoamylase Multifect GA 10L show the most acceptable results in comparison with the normal enzymatic desizing carried out at pH 5 and also the blank samples. At pH 5 there was no great different between the enzymes used. Almost all the enzymes in the given conditions removed the size. The best results were obtained by using the mixture of Glucoamylase Multifect GA 10L and Optisize Next even in 60 ^{o}C or at room temperature. The increase in concentration of enzymes from 8 ml/l to 16 ml/l did not cause a great change in the final results. Regarding to the temperature effect on the results of enzymatic desizing carried out at pH 5, some enzymes showed better performance in 60 ^{o}C, including Optisize HT plus, in which weight loss increased from 8.41 to 10.23%, drop test decreased from 00:23 to 00:08 and starch detection has improved from 6 to 7-8, in the same concentration of enzymes (8 ml/l).

In the case of enzymatic desizing at pH 2, the effect of temperature and concentration of enzymes were more significant. Desizing at pH 2 is an acidic desizing, thus increasing of temperature from room temperature to 60 ^{o}C could

lead to increase in rate of acidic denaturalizing of enzymes (Cavaco- Paulo & Gübitz, 2003). On the other hand, more concentration of enzymes in higher temperature (60 ^{o}C) showed a better effect, because in higher temperatures enzymes will be hydrolyzed rapidly. Consequently increase of enzymes concentration can reduce the rate of acidic hydrolyzing (Cavaco- Paulo & Gübitz, 2003).

Furthermore, the presented data in Tables 1.6.1 and Table 1.6.2 indicate that application of a glucoamyase and α-amylase in a same time led to better desizing performance, specially the mixture of glucoamylase Multifect GA 10L and α-amylase Optisize Next. This is due to the synergistic action of glucoamyase and α-amylase in hydrolysis of starch. Basically enzymatic hydrolysis of starch is accomplished by two types of enzymes: endoenzymes (mainly α-amylase) break down the starch molecule randomly into smaller molecules such as oligosaccharides and exoenzymes (mainly glucoamylase) cleave α-1, 4 and α-1, 6 linked glucose from starch (Coutinho & Reilly, 1997; Fujii & Kawamura, 1985; Van der Maarl et al. 2002; Roles & Delft, 1979; Vrsalović Presečki et al. 2009).

Although use the mixture of two enzymes means doubling the total concentrations of enzymes in the process, the results show that doubling of enzymes individually (16 ml/l instead of 8 ml/l for each enzyme) has not caused a significant increase in desizing grade. Therefore, enzymatic desizing at pH 2 and room temperature by the mixture of two enzymes, in which glucoamylase had more resistance against acid hydrolyzing, caused a sufficient elimination of starch. By application of a mixture of two enzymes at pH 2, the absorbency of cotton samples improved from 7 min (on average) to 8 sec, after 60 min and from 6 min to 3 sec when the desizing was done overnight. Increase of absorbency is mainly caused by the decomposition of hydrophobic molecules of starch to the smaller monosaccharaides and oligosaccharides (Coutinho & Reilly, 1997; Fujii & Kawamura, 1985; Van der Maarl et al. 2002; Roles & Delft, 1979; Vrsalović Presečki et al. 2009).

The other factor which should be considered, is the temperature. Table 1.6.1 shows that in the case of desizing in acidic conditions, the rate of acidic hydrolyzing of

enzyme(s) will be more, thus desizing at room temperature may be more successful.

It can be concluded that the best acid-stable enzyme(s) and the best conditions of processing for a successful enzymatic desizing under acidic conditions are: α-amylase Optisize Next and its combination with glucoamylase Multifect GA 10L, preferably in room temperature.

For an easier comparison of the obtained results from enzymatic desizing, the overall results of desizing with Optisize Next, Multifect GA 10L and their mixture at pH 2 and pH 5 from the Tables 1.6.1 and Table 1.6.2 are summarized into three graphs: starch-detection based on TEGEWA, drop test and weight loss. Also for an easier analyzing, in these graphs just room temperature as the process temperature and overnight as the process time were selected. The concentration of 8 ml/l was the selected concentration.

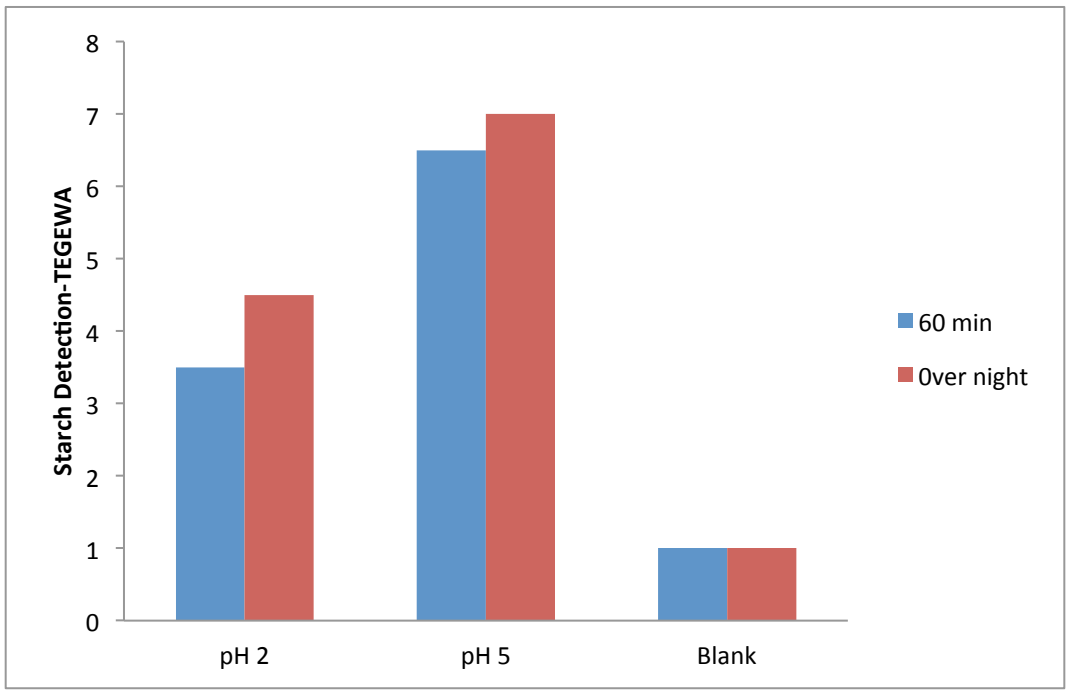

Figure 1.6.1 Starch detection test of desized cotton with Optisize Next (8 ml/l, room temperature)

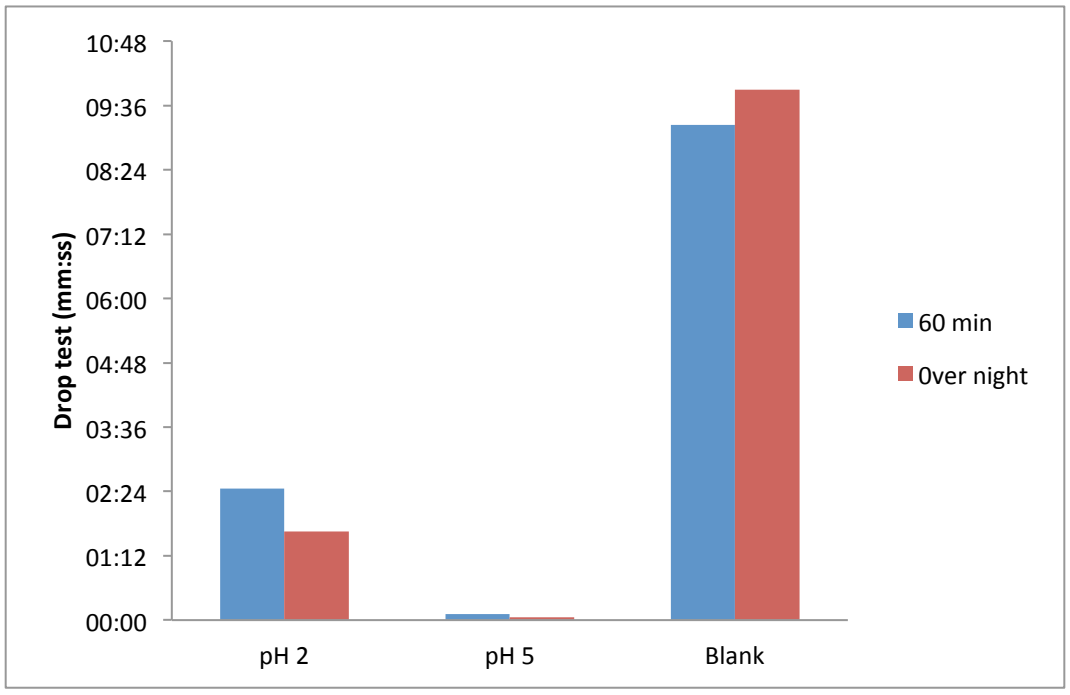

Figure 1.6.2 Drop test of desized cotton with Optisize Next (8 ml/l, room temperature)

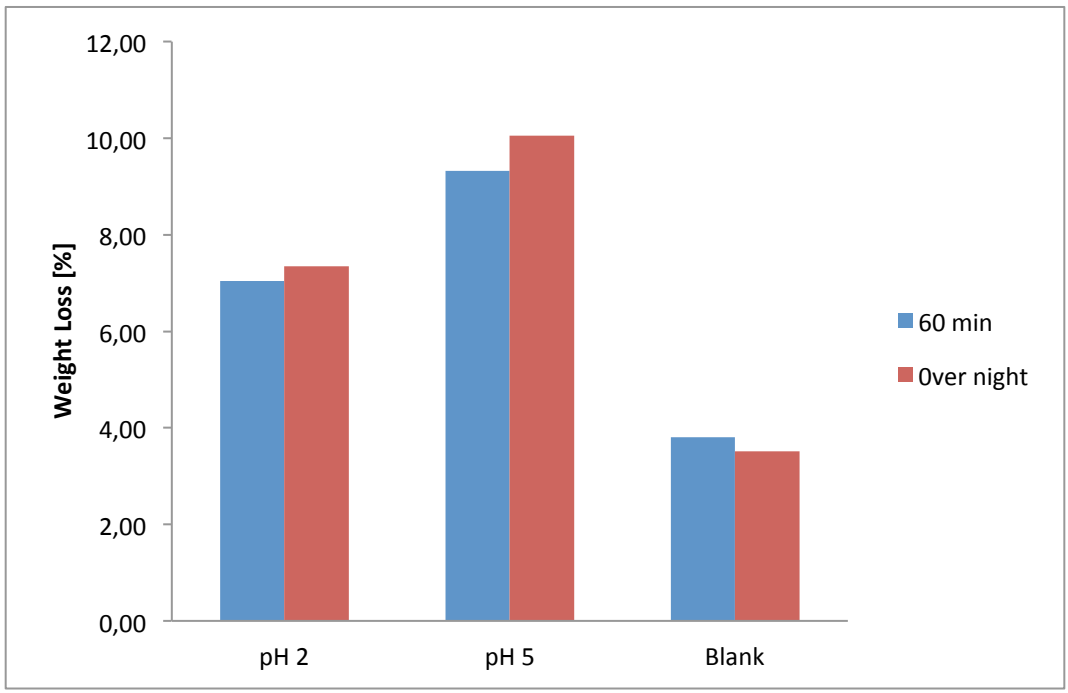

Figure 1.6.3 Weight loss (%) of desized cotton with Optisize Next (8 ml/l, room temperature)

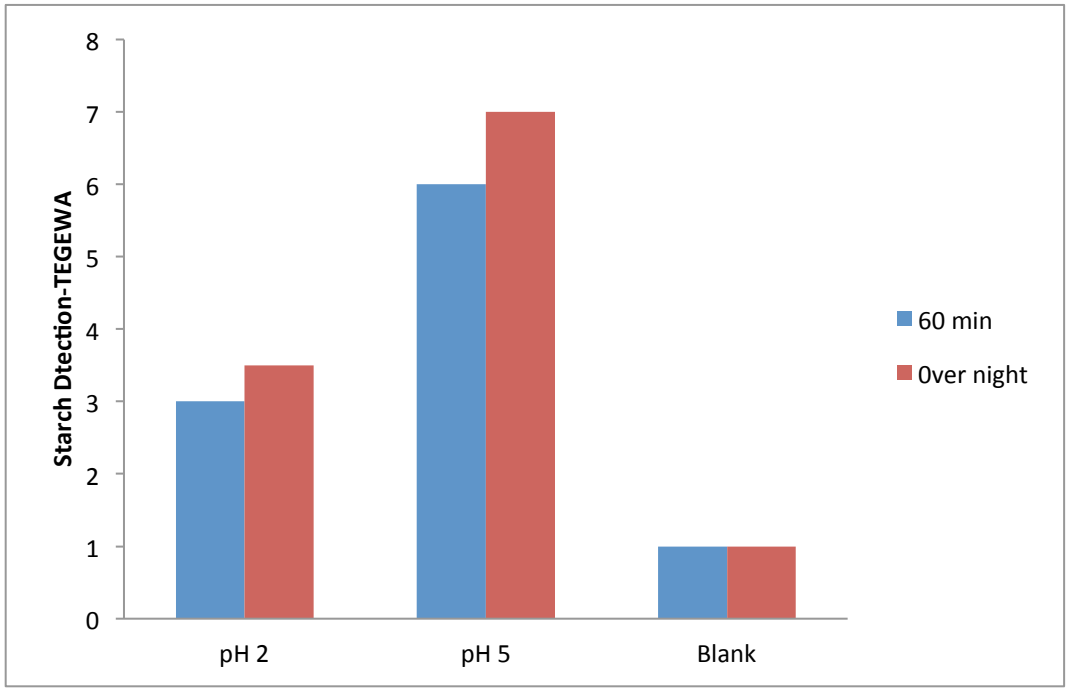

Figure 1.6.4 Starch detection test of desized cotton with Multifect GA 10L (8 ml/l, room temperature)

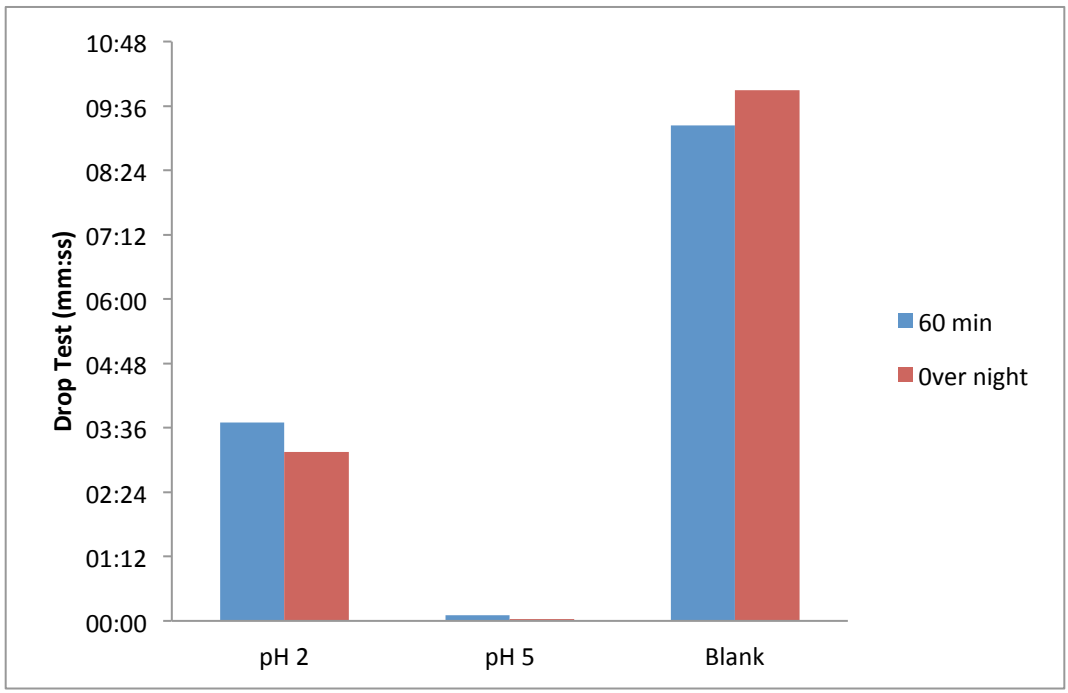

Figure 1.6.5 Drop test of desized cotton with Multifect GA 10L (8 ml/l, room temperature)

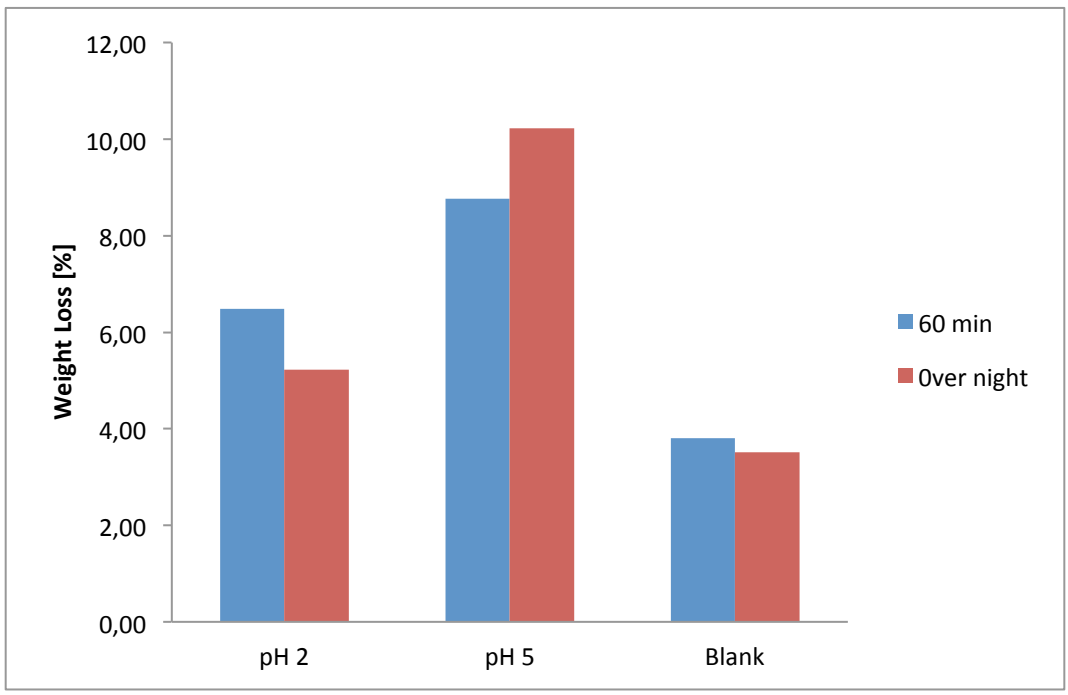

Figure 1.6.6 Weight loss (%) of desized cotton with Multifect GA 10L (8 ml/l, room temperature)

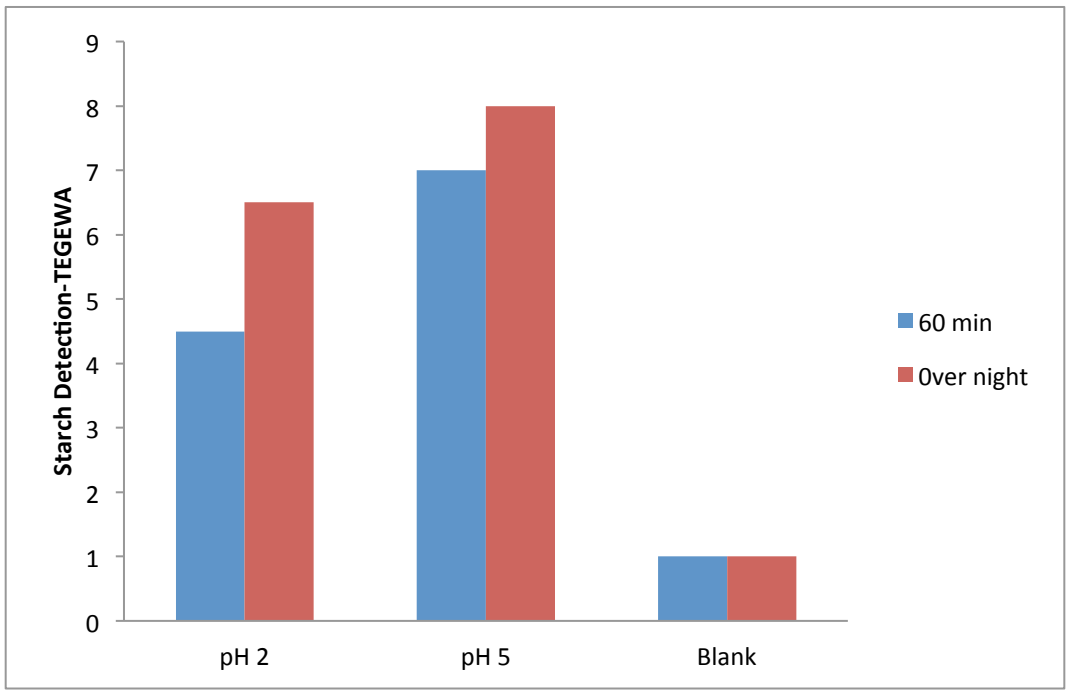

Figure 1.6.7 Starch detection test of desized cotton with Optisize Next + Multifect GA 10L

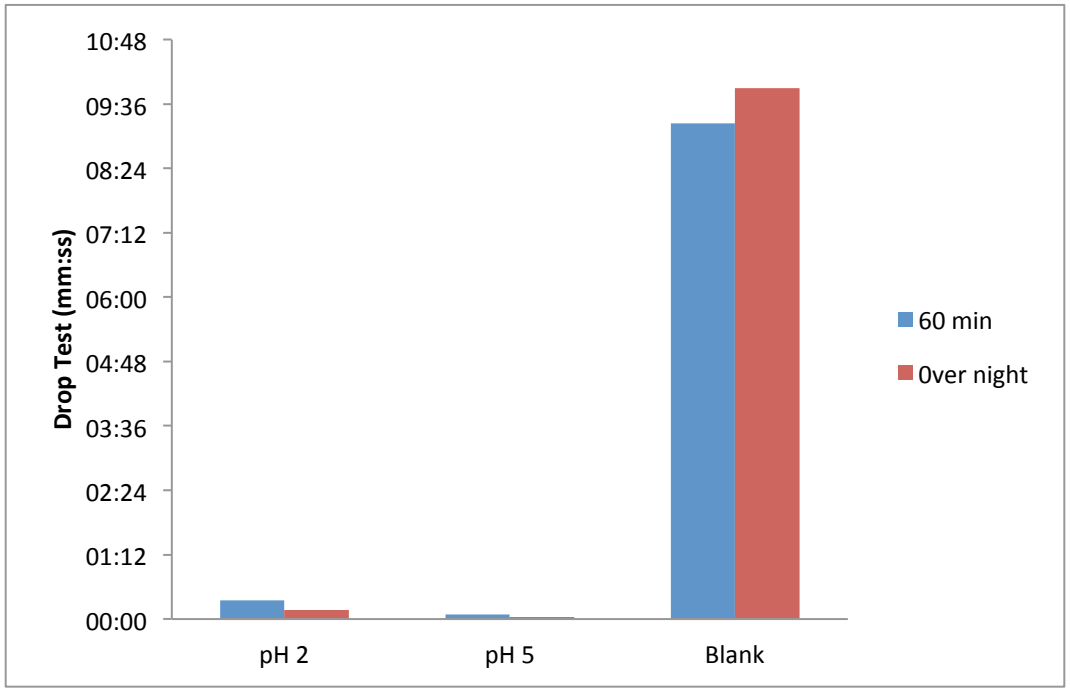

Figure 1.6.8 Drop test of desized cotton with Optisize Next + Multifect GA 10L

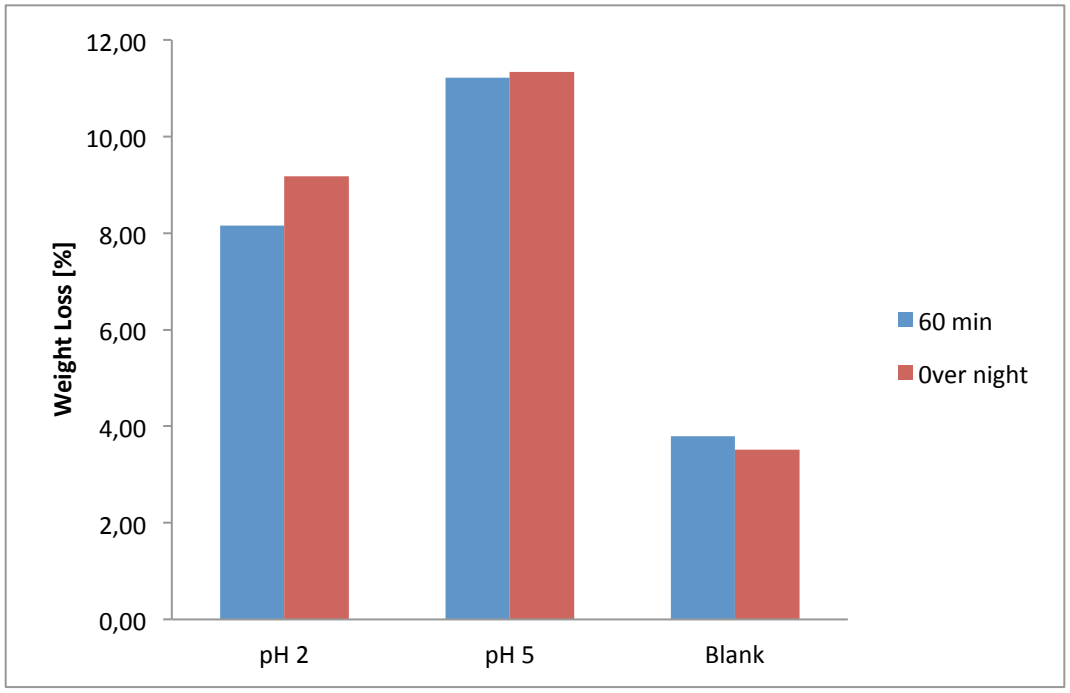

Figure 1.6.9 Weight loss (%) of desized cotton with Optisize Next+Multifect GA 10L

It is observed that there is a good correlation between the results of different indicators. Using a mixture of two enzymes at pH 2, the absorbency of cotton samples improved from 7 min (on average) to 8 sec, after 60 min and from 6 min to 3 sec when the desizing was done overnight. Increase of absorbency is mainly caused by the decomposition of hydrophobic molecules of starch to the smaller monosaccharaides and oligosaccharides (Coutinho & Reilly, 1997; Fujii & Kawamura, 1985; Van der Maarl et al. 2002; Roles & Delft, 1979; Vrsalović Presečki et al. 2009).

Increase of weight loss of the pretreated samples by the mixture of two acid stable enzymes at pH 2 from 3% (averagely) to about 11% is another indicator of a relative successful desizing under the given conditions. The highest weight loss was obtained from the desized samples at pH 5, when the mixture of two enzymes was employed. Compared to these results, the weight loss of desized cotton at pH 2 was more than 10%, which indicates a satisfactory desizing. Three factors: degree of desizing, absorbency and weight loss of desized samples (after 60 min and or overnight) at pH 2 demonstrated a very good correlation. In comparison to the

enzymatic desizing at pH 5, a sufficient desizing at pH 2 was achievable using the mixture of acid-stable glucoamylase (Multifect GA 10L) and α-amylase (Optisize Next), when they were employed at room temperature and the process completed overnight.

1.6.2 Using chelating agents in enzymatic desizing

After analyzing the different enzymes and the practical conditions of enzymatic desizing, especially in pH 2, and finally selection of the best acid stable enzymes from the available industrial enzymes, the next stage was to investigate the performance of acid-demineralization. There are basically two ways to eliminate minerals and cationic metal cations: generating more soluble salts e.g. acid-demineralization and use of sequestering agents (Karmakar, 1999; Hvattum & Turner, 1951). Practically, a combination of acid- demineralization and sequestering agents is applied in textile industry in order to remove the metals effectively and uniformly. In this way, catalytic damaging which is originated from peroxide bleaching will be minimized. Moreover, acid-demineralization can reduce the possible accumulation of hardly soluble earth alkalis (Karmakar, 1999). Even and more brilliant dyeing and also reducing the amounts of peroxide used are the other benefits (Karmakar, 1999; Trotman, 1970).

To achieve an acceptable performance of acid-demineralization, enzymatic desizing with the selected enzymes was carried out one more in presence of a chelating agent Beixon NE and a nonionic surfactant Flosan NKB. Every enzymatic desizing was done with 8 ml/l of enzyme, at room temperature. The results are summarized in Table 1.6.3 and Table 1.6.4.

Table 1.6.3 Starch detection-TEGEWA method

		Multifect GA 10L		Optisize Next		Multifect GA 10L+Optisize Next		Blank	
		60 min	over night	60 min	over night	60 min	over night	60 min	over night
pH 2	With ChA[a]	3	4	3-4	4-5	4-5	6-7	1	1
	Without ChA	3	3-4	3	4	4-5	6	1	1
pH 5	With ChA	6	7	6-7	7-8	6-7	8-9	1	1-2
	Without ChA	6	7	6-7	7	6-7	8	1	1-2

[a] chelating agent

Table 1.6.4 Drop test-TEGEWA method and weight loss of cotton samples before and after desizing

		Multifect GA 10L (8 ml/l)				Optisize Next (8 ml/l)				Multifect GA 10L+Optisize Next				Blank			
		60 min		over night		60 min		over night		60 min		over night		60 min		over night	
		DT[b]	WL[c]	DT	WL	DT	WL	DT	WL	DT	WL	DT	WL	DT	WL	DT	WL
pH 2	With ChA[a]	02:23	6.94	02:05	7.16	02:01	7.23	01:02	7.92	00:08	9.09	00:03	10.47	07:23	3.69	06:14	3.8
	Without ChA	03:42	6.48	03:09	6.52	02:27	7.04	01:39	7.34	00:21	8.16	00:10	9.18	09:37	2.75	08:53	2.77
pH 5	With ChA	00:05	9.31	00:01	10.55	00:04	9.67	00:02	10.27	00:03	9.88	00:01	11.67	08:08	4.00	07:01	4.06
	Without ChA	00:06	8.77	00:02	10.23	00:07	9.32	00:03	10.05	00:05	10.18	00:02	11.22	10:11	3.22	09:45	3.51

[a] chelating agent

[b] drop test (mm:ss)

[c] weight loss (%)

The presence of chelating agent in enzymatic desizing had no negative effect on the performance of desizing. On the other hand, a little improvement in performance of desizing in the presence of chelating agent was seen. A slight increase in starch-detection scale (TEGEWA-method) and weight loss and also a light decrease in drop penetration time of desized samples in the presence of chelating agent illustrated this fact. This slight improvement may also originate from the nonionic surfactant. Actually distinguishing between these two factors was not easy and also was not the purpose of the study.

For an easier analyzing, the results of Tables 1.6.3 and 1.6.4 are plotted in graphs (Figure 1.6.10 - Figure 1.6.19), according to three analyzing factors: starch detection TEGEWA-test, drop test and weight loss. For evaluation of desizing all three defined factors should assessed in a same time.

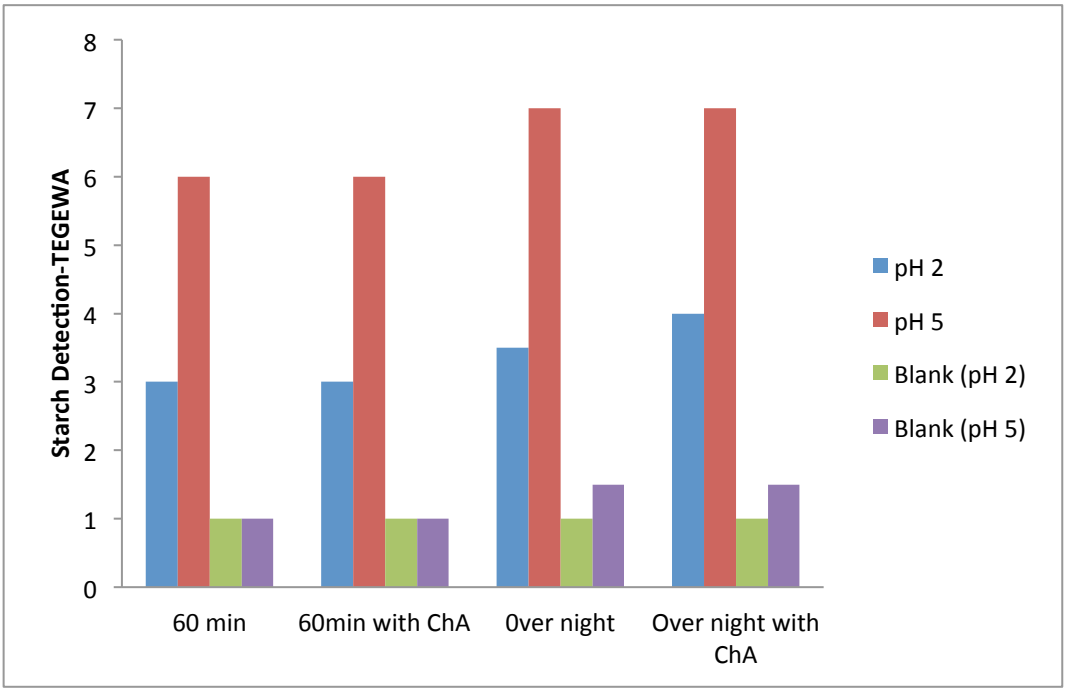

Figure 1.6.10 Results of starch detection test for samples desized with Multifect GA 10L, in presence or absence of chelating agent and nonionic surfactant

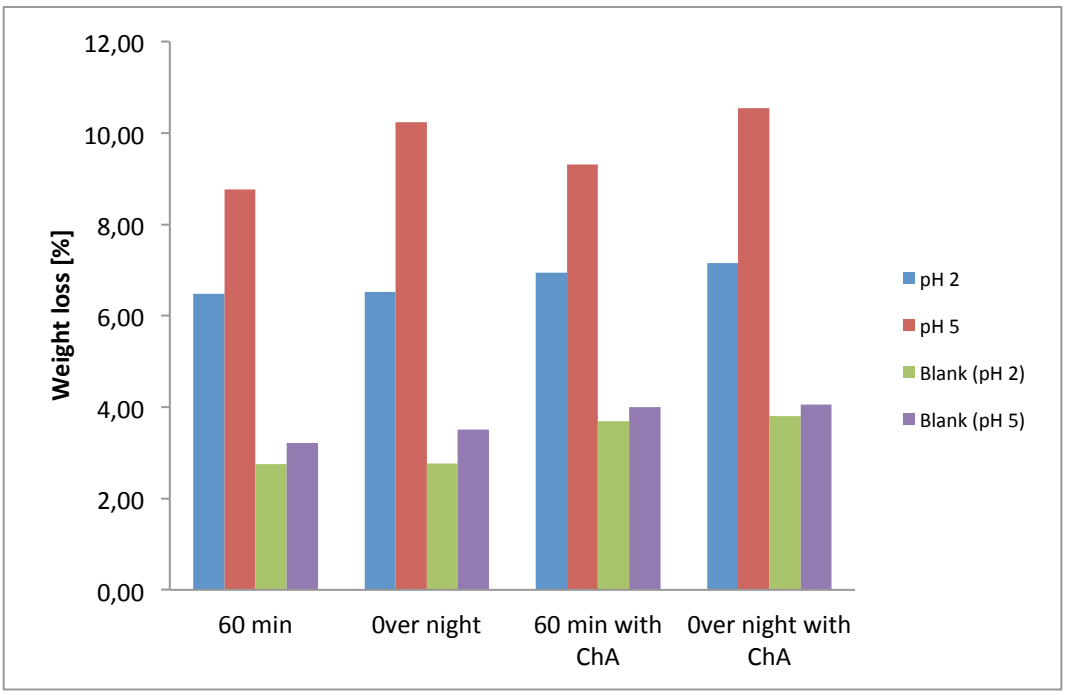

Figure 1.6.11 Weight loss (%) of samples desized with Multifect GA 10L, in presence or absence of chelating agent and nonionic surfactant

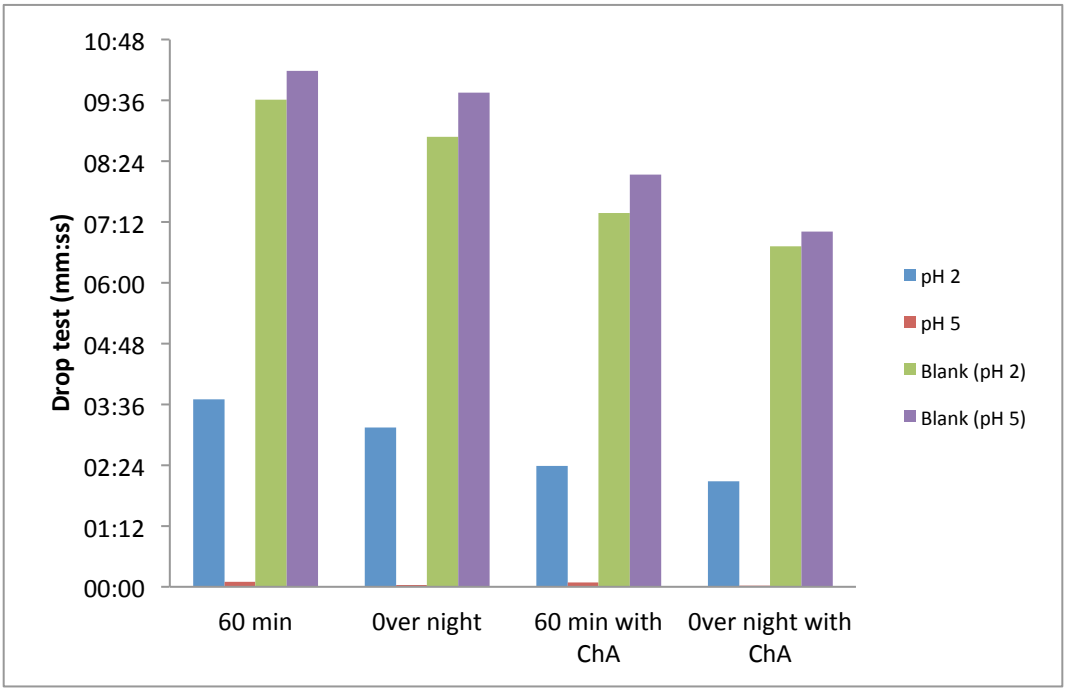

Figure 1.6.12 Results of drop test for samples desized with Multifect GA 10L, in presence or absence of chelating agent and nonionic surfactant

Figures 1.6.10, 1.6.11 and 1.6.12 show that the presence of chelating agent and nonionic surfactant does not have any impact on efficiency of desizing with glucoamylase Multifect GA 10L. Also a slight improvement in overall performance of desizing with this enzyme in the presence of chelating agent and nonionic surfactant can be seen. Increase of TEGEWA indicators and weight loss and decrease in drop test indicate the positive impact of added auxiliaries.

In Figures 1.6.13, 1.6.14 and 1.6.15 the same trend are seen, when α-amylase Optisize Next was used.

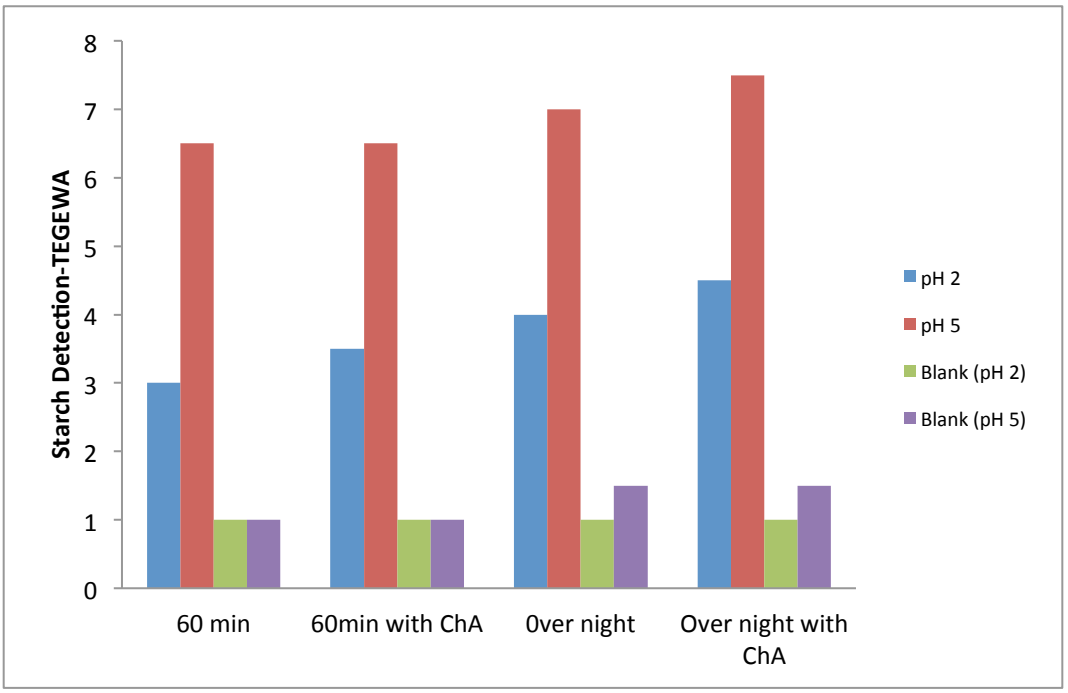

Figure 1.6.13 Results of starch detection test for samples desized with Optisize Next, in presence or absence of chelating agent and nonionic surfactant

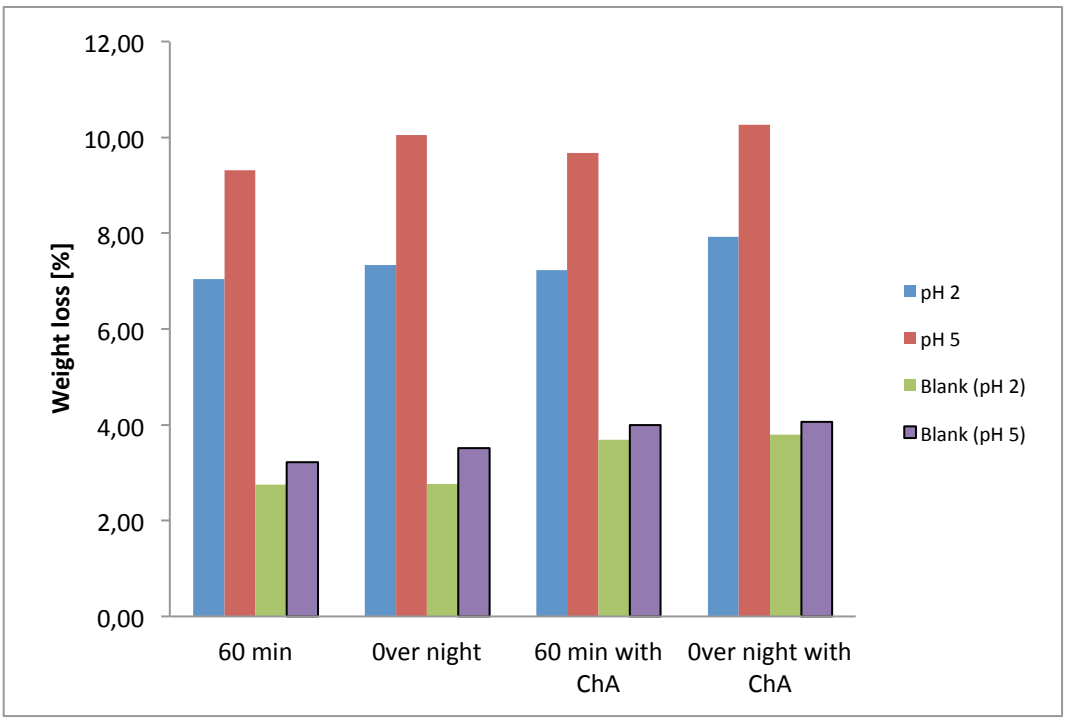

Figure 1.6.14 Weigh loss (%) of samples desized with Optisize Next, in presence or absence of chelating agent and nonionic surfactant

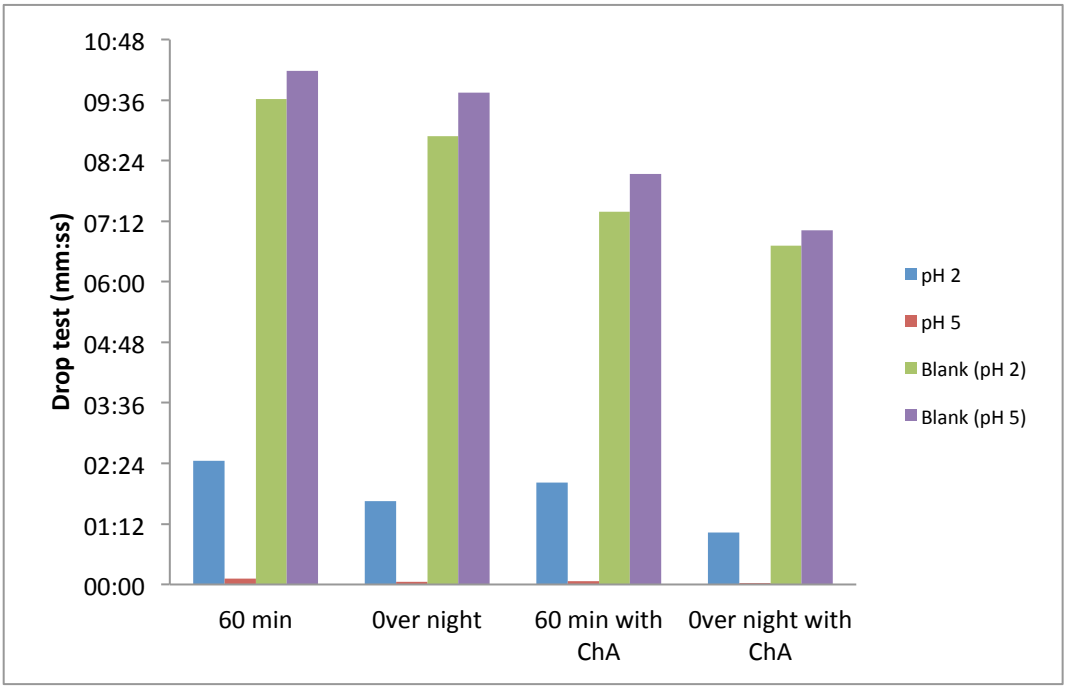

Figure 1.6.15 Results of drop test for samples desized with Optisize Next, in presence or absence of chelating agent and nonionic surfactant

As it can be seen, when the α-amylase Optisize Next employed, chelating agent and nonionic surfactant helped to improve the efficiency of enzymatic desizing. However, as like as the case of Multifect GA 10L, enzymatic desizing at pH 5 led to better results.

When the mixture of two enzymes (Multifect GA 10L+Optisize Next) was used, also the similar trend was seen. Presence of the chelating agent and the nonionic surfactant helped to improve the performance of enzymatic desizing (see Figures 1.6.16-1.6.18).

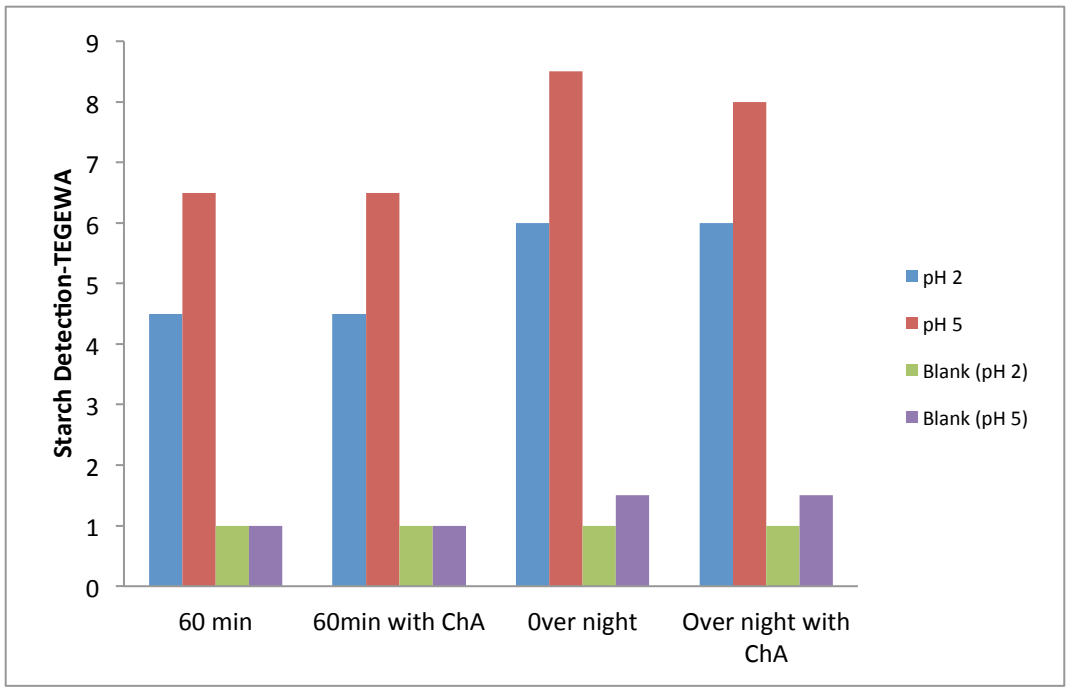

Figure 1.6.16 Results of starch detection test for samples desized with mixture of Multifect GA 10L and Optisize Next, in presence or absence of chelating agent and nonionic surfactant

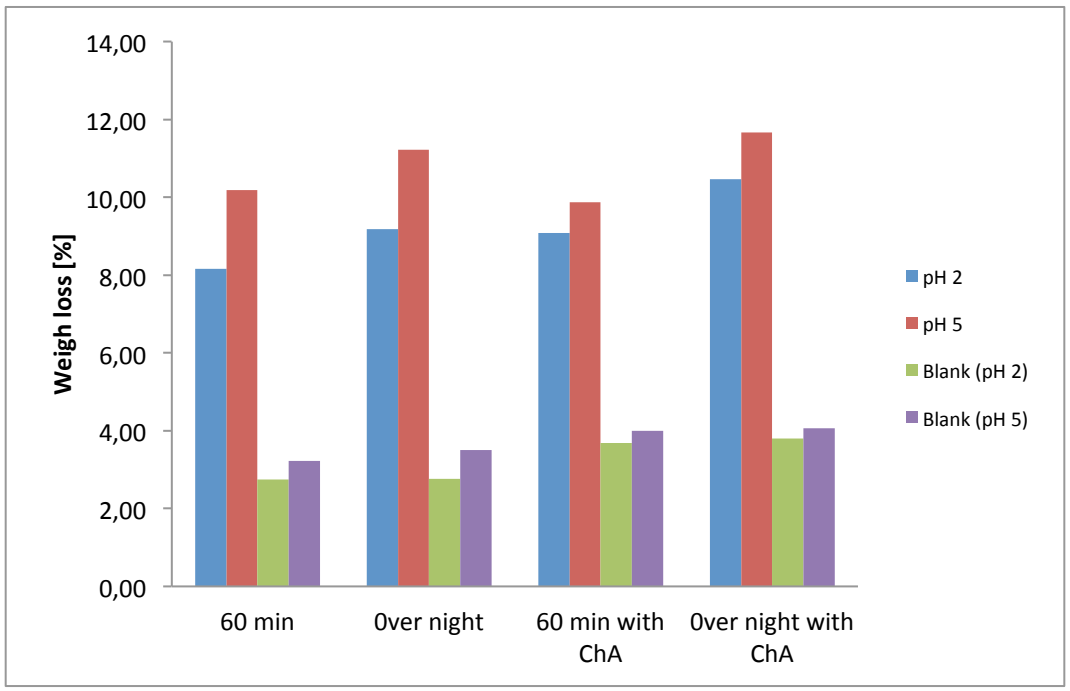

Figure 1.6.17 Weight loss (%) of samples desized with mixture of Multifect GA 10L and Optisize Next, in presence or absence of chelating agent and nonionic surfactant

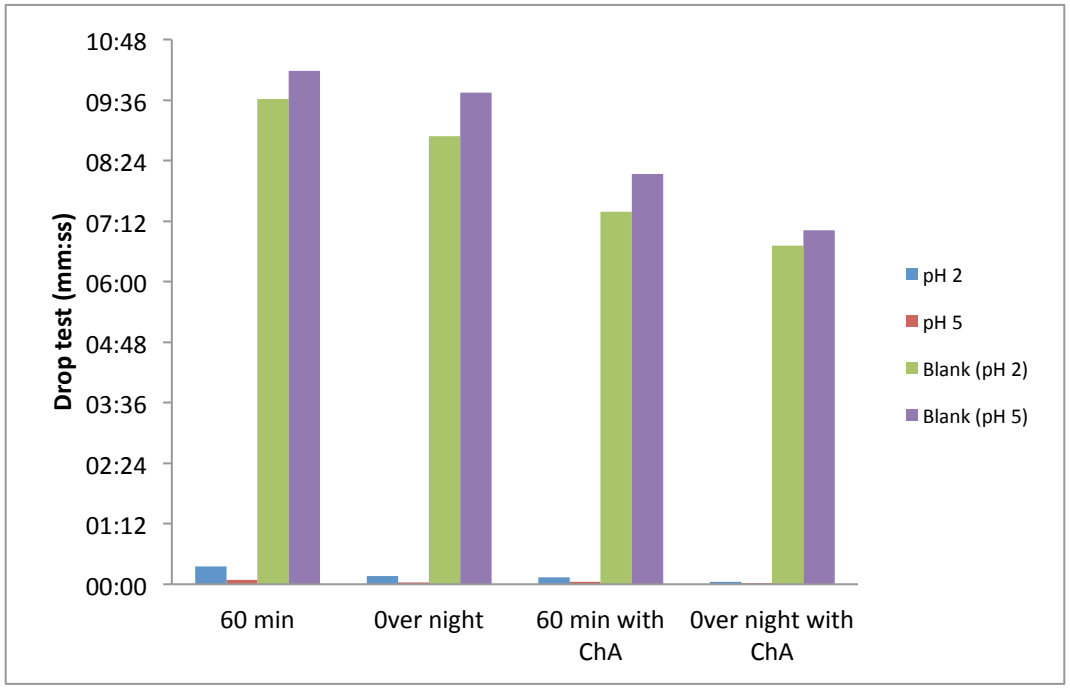

Figure 1.6.18 Results of drop test for samples desized with mixture of Multifect GA 10L and Optisize Next, in presence or absence of chelating agent and nonionic surfactant

1.6.3 Measurement of the remaining cationic metals

Concentrations of remaining cationic metals in the enzymatic desized samples were measured, which were desized by the mixture of enzymes at pH 2 and pH 5. The results are presented in Figures 1.6.19-1.6.26 and different conditions of processes (pH 2 and pH 5 with or without chelating agent, in the presence or absence of enzymes) were compared. Also the concentration of cationic metal in original cotton fabric (raw cotton) is shown.

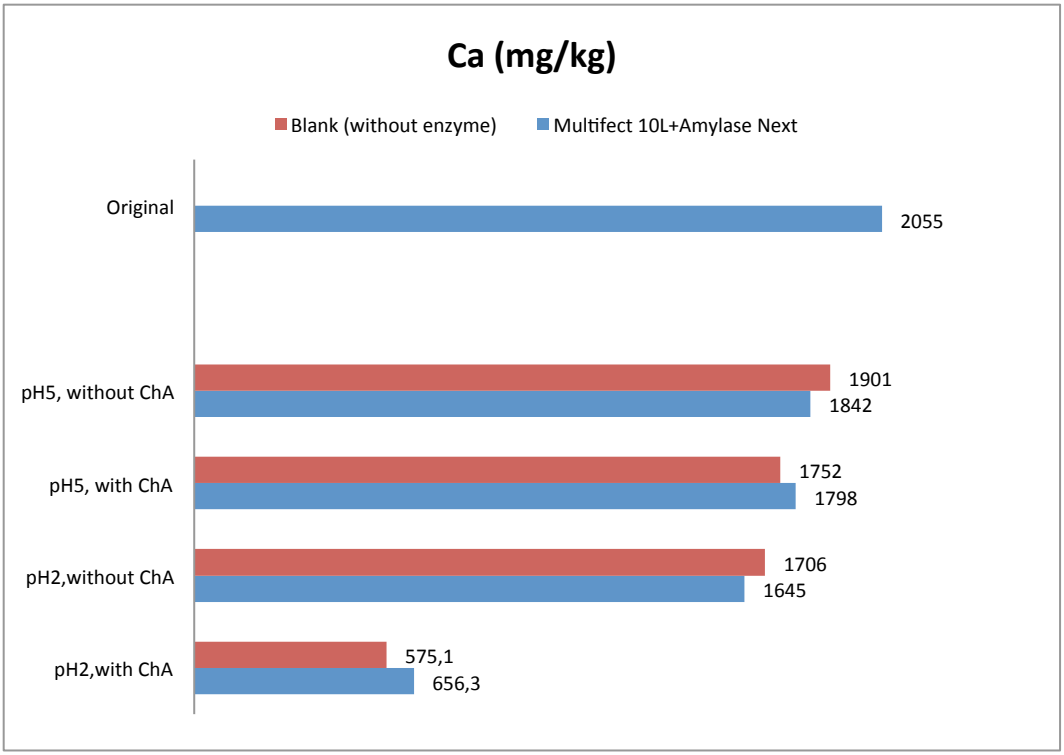

Figure 1.6.19 Concentration of calcium in cotton samples

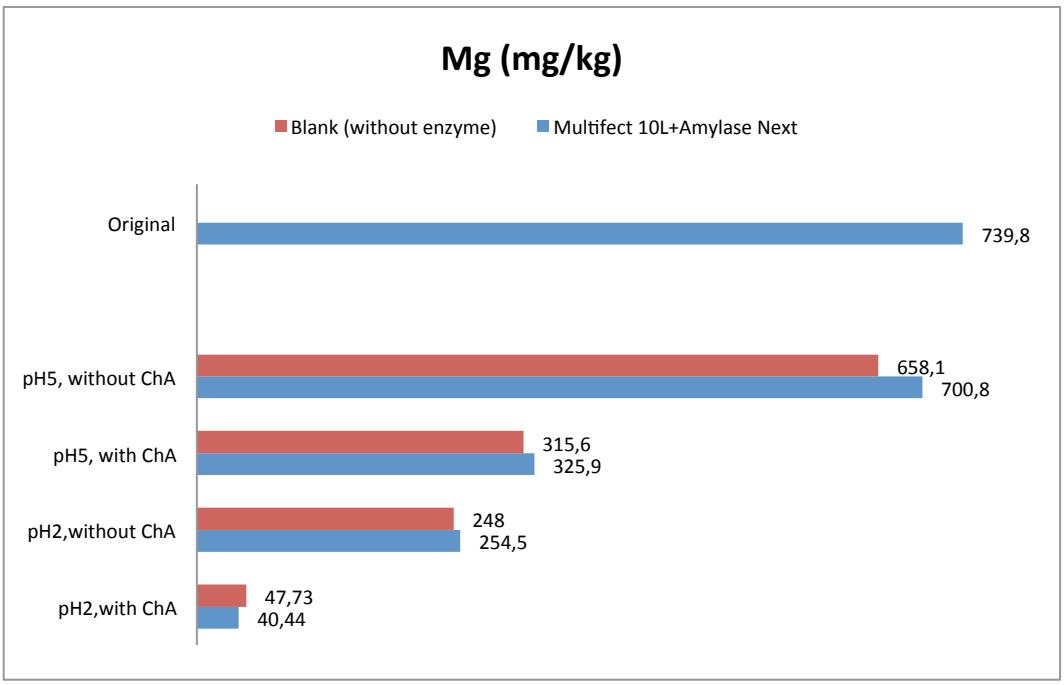

Figure 1.6.20 Concentration of magnesium in cotton samples

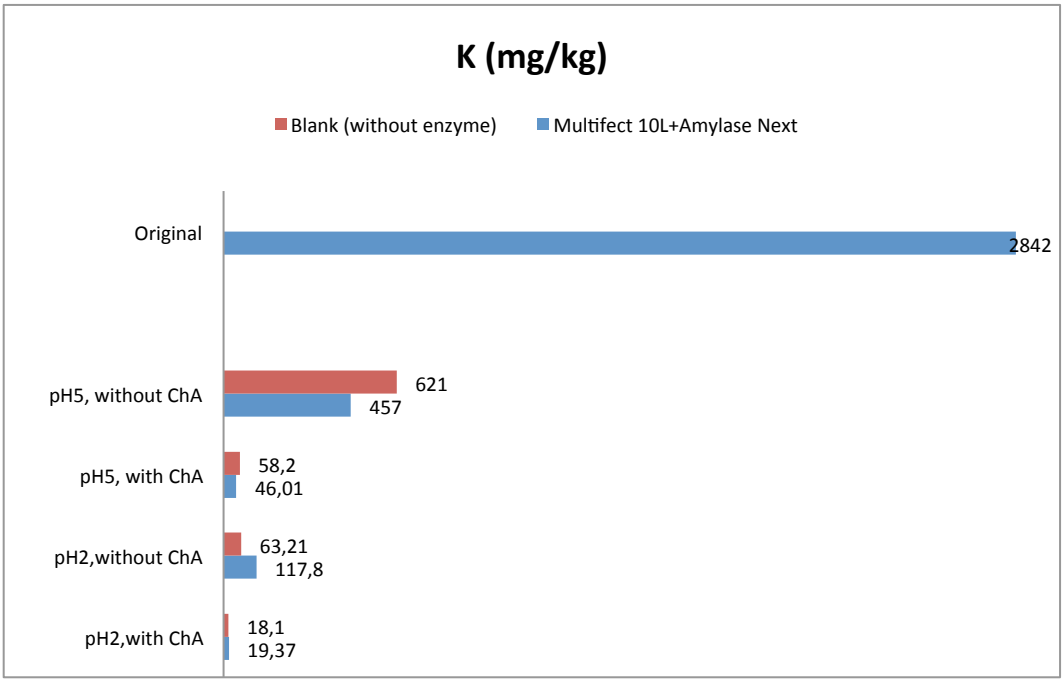

Figure 1.6.21 Concentration of potassium in cotton samples

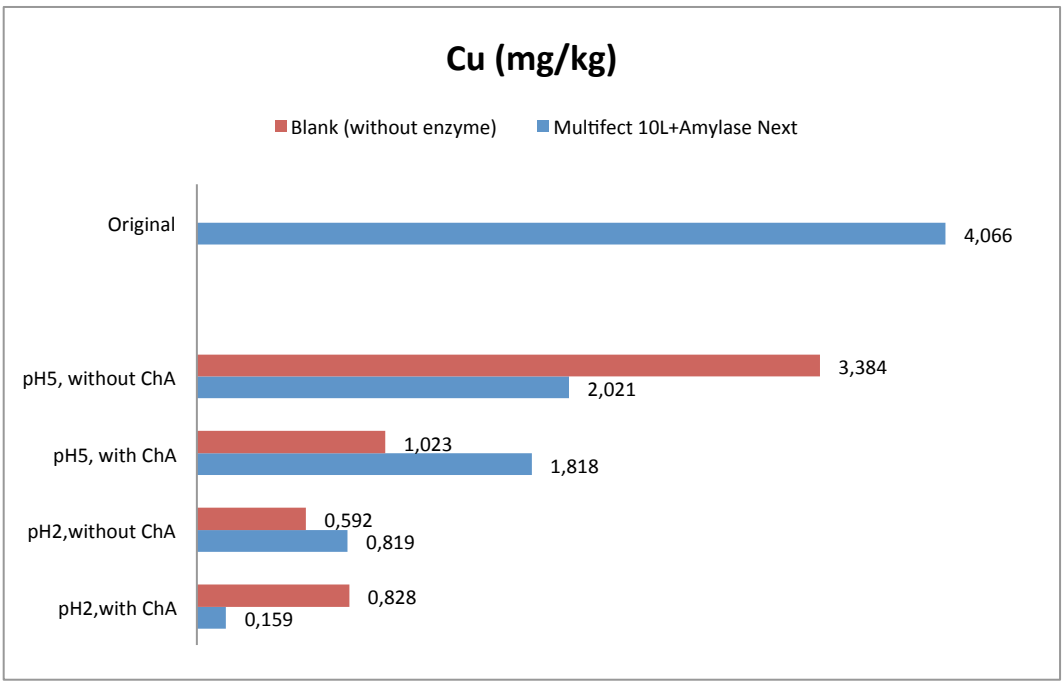

Figure 1.6.22 Concentration of copper in cotton samples

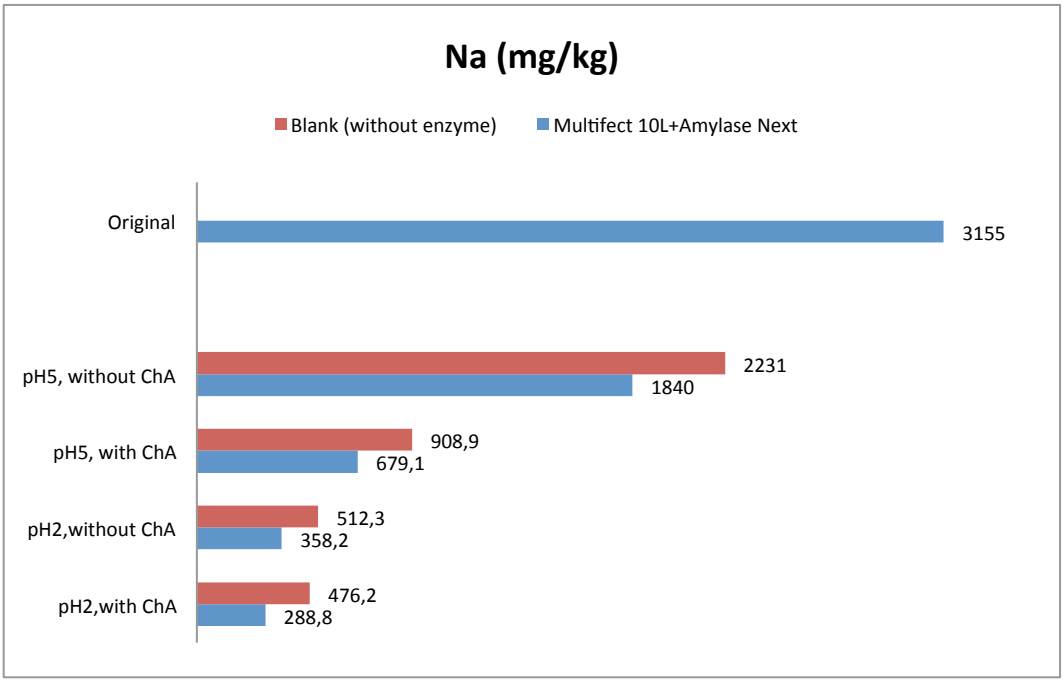

Figure 1.6.23 Concentration of sodium in cotton samples

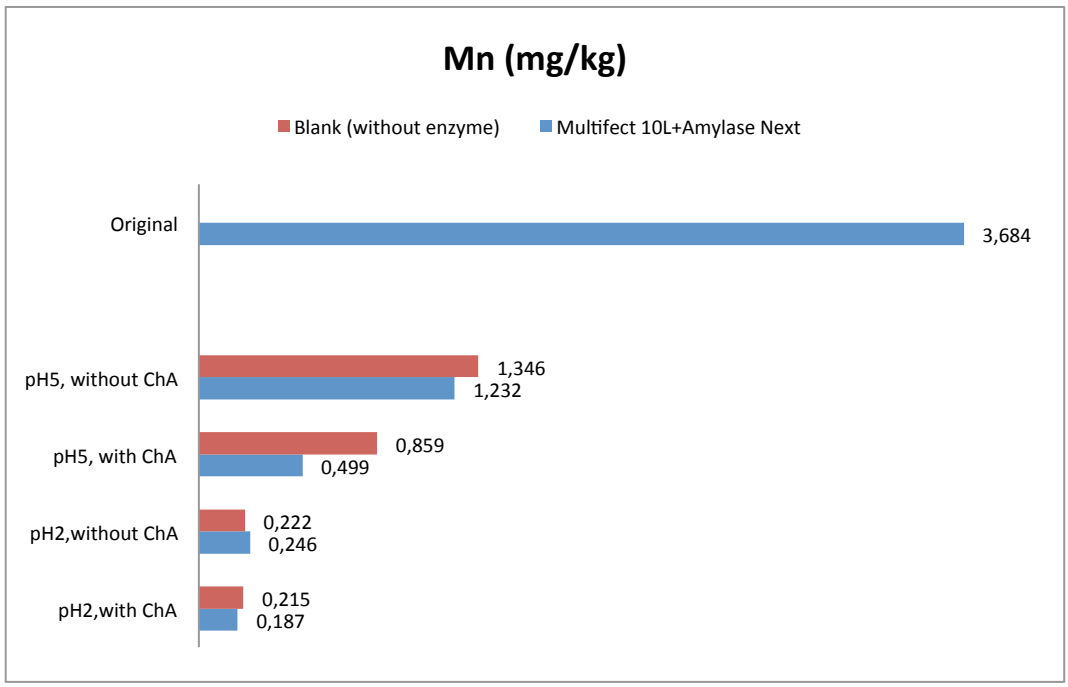

Figure 1.6.24 Concentration of manganese in cotton samples

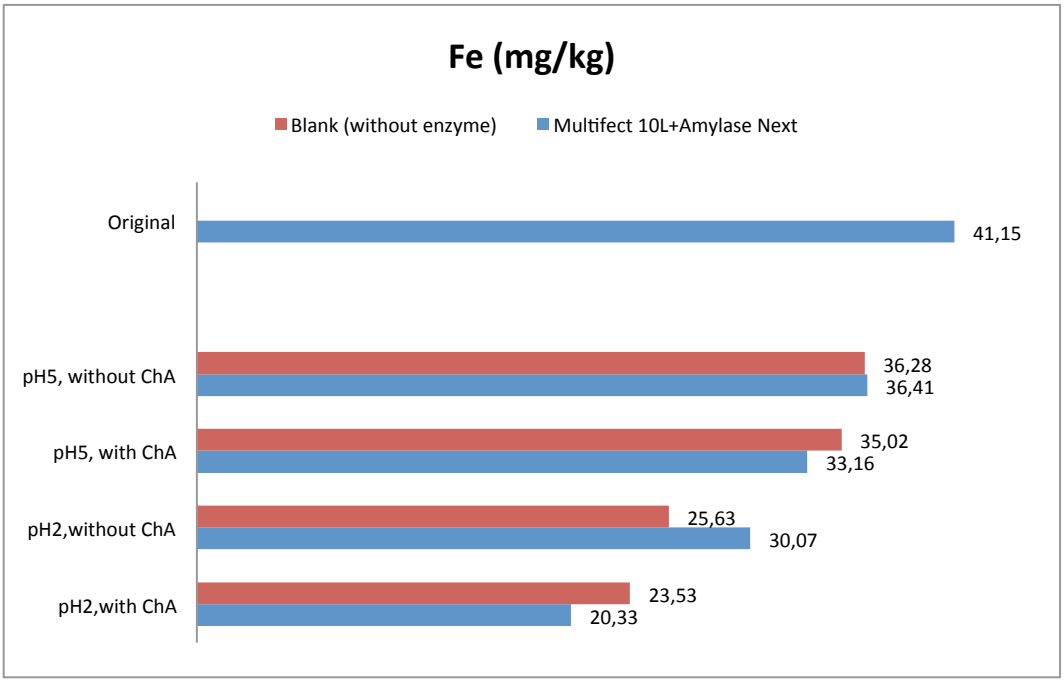

Figure 1.6.25 Concentration of iron in cotton samples

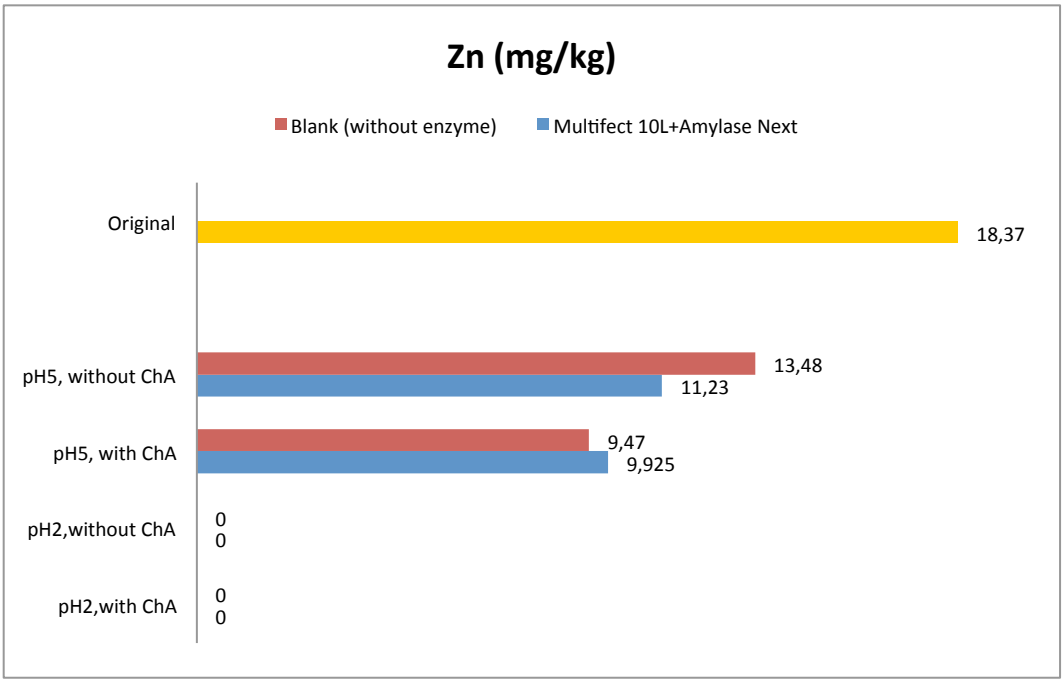

Figure 1.6.26 Concentration of zinc in cotton samples

The results show that acid-demineralization of cotton fabrics at pH 2 was successfully performed. Potassium, copper, manganese, magnesium, zinc and sodium were almost completely removed. Concentration of potassium from 2842 mg/kg in original sample was reduced to about 18 mg/kg in enzymatic desized cotton sample in presence of chelating agent at pH 2 and about 63 mg/kg in the same conditions but in absence of chelating agent. It means that potassium was removed effectively and also it indicates the positive role of chelating agent under acidic condition for removing of potassium. Also in non-acidic condition, i.e. pH 5, chelating agent alone could eliminate the potassium.

Similar results were obtained in the case of magnesium, sodium, copper, manganese and zinc. Concentration of magnesium from 739.8 mg/kg in original sample has been reduced to about 40 mg/kg in the enzymatic desized cotton at pH 2 in presence of the chelating agent. In this case, the chelating agent helped to remove the magnesium from the cotton (concentration of magnesium in desized sample at pH 2 without chelating agent was ca. 250 mg/kg, about 6 times more than the same conditions but in presence of chelating agent). On the other side, in

desizing at pH 5 chelating agent has not caused to remove magnesium. It indicates that, in the case of magnesium acidic condition is more effective than chelating agent to eliminate this cation. The concentration of sodium has been decreased from 3155 mg/kg to 288.8 mg/kg in the enzymatic desized cotton at pH 2 in the presence of chelating agent. Concentration of copper was reduced from 4.066 mg/kg to 0.159 mg/kg in the desized cotton under the acidic conditions. The concentration of manganese in the raw sample was 3.684 mg/kg, which was reduced to 0.187 mg/kg in the enzymatic desized cotton at pH 2. Zinc was completely removed, as its concentration from 18.37 mg/kg in the raw sample was decreased to 0.00 mg/kg.

However, the amount of demineralized calcium and iron is not acceptable, because about half and quarter of the original amounts of calcium and iron were demineralized. A good pretreated cotton fabric should have 100-300 mg/kg of calcium and 4-8 mg/kg of iron (Karmakar, 1999). Thus, the degree of demineralization of iron and calcium is not acceptable. Even using of a chelating agent did not help effectively to remove iron and calcium. This may originate from the low temperature of process or weakness of the acid used. It has been found that use of a chelating agent at a higher pH (pH 5) did not remove the cationic metals completely. It means that for a simultaneously demineralization and desizing reducing pH to less than 3 is necessary. The presence of chelating agent in the desizing process at pH 5 partially removed the existing cationic metals in cotton, but not as sufficient as required. In the case of zinc, demineralization was successfully done at pH 2 even without chelating agent. Unlike zinc, elimination of potassium was more affected by the presence of chelating agent. Even at pH 5 chelating agent could effectively remove potassium.

2

Multifunctional Finishing of Cotton Fabrics Using Carboxylated Polyamines

2.1 Introduction

Chemical or wet processing of textiles can be basically divided into three stages: pretreatment, dyeing and finishing. Dyeing process is the application of dyestuffs into textile materials to produce a colored textile. Finishing provides extra properties for textiles that customers will value. In the other word, finishing is completing the fabric's performance by providing special functions. However, there are some more general and broader definitions: "Any operation for improving the appearance or usefulness of a fabric after it leaves the loom or knitting machine can be considered a finishing step" (Tomasino 1992). Concerning this definition, pretreatment processes such as washing and bleaching should be considered as the finishing stages. Nevertheless, in this thesis finishing is used in a more restricted definition, which considers all processes to add extra values such as fashion aspects and new functions into the textile materials.

There is also another classification of textile finishing: chemical or wet finishing and mechanical finishing. The chemical finishing involves the addition of some chemicals to a textile material to provide the desired effect. The properties such as flame retardancy and easy-care can be achieved by chemical finishing. The chemical finishing of textile material will definitely change the chemical composition, but the appearance is usually unchanged. The mechanical finishing or dry finishing includes physical means to change fabric properties, such as heat setting or plasma irradiation (Schindler & Hauser, 2004; Rouette 2001).

The most conventional and important chemical finishing processes are: softening finishing, hand building finishing, easy-care or durable press finishing of cellulosic fabrics, repellent finishing, soil-release finishing, flame-retardant finishing, non-slip finishing, antistatic finishing, anti-pilling finishing, elastomeric finishing, ultraviolet protection finishing, antimicrobial finishing, insect resist and mite protection finishing, anti-odor and fragrance finishing and surface modification of textiles by sol-gel finishing with inorganic oxide films (Schindler & Hauser, 2004; Rouette 2001).

Setting a suitable formulation in the chemical finishing requires considering of several important factors (Schindler & Hauser, 2004):

- type of textile (fiber and construction)
- extent of effect and durability of the desired performance
- economic benefits and costs
- restriction imposed on the process (procedure requirement)
- environmental consideration
- compatibility of the formulation with other chemicals

An effective and successful chemical finishing should bring all the mentioned factors, which is not easy. Also, due to the economic reasons several types of finishes are combined into a single stage, which makes more challenges to consider the above-mentioned factors. However, textile industry tends to utilize the combination of finishing processes in a single bath or at least reducing the number of necessary stages to decrease the costs of production. Using multifunctional finishing seems as one of the most attractive means in textile industry. This idea has been tried by some researchers to provide more effects in a finished fabric just in a single bath. For example, Qing and his colleagues investigated a molecule which contains both perfluoroalkyl-containing multifunctional groups as suitable finishing agent for fabrics with wrinkle resistance, water repellency, oil repellency and soil repellency (Qing, et al. 2002), or the researches of Chung, Lee, and Kim for simultaneously durable press and antimicrobial finishing of cotton fabrics with a combination of citric acid and chitosan (Chung et al. 1998).

Multifunctional finishing is even more important for cotton textiles, because cotton is the most important kinds of fabrics in apparel industry. This importance and desirability in garments is due to the unique property of this natural fiber. Since cotton can readily absorb moisture, the cotton made clothes are the most comfortable garments. But easy wrinkling of cotton garments is their main disadvantage. On the other hand, there is always an increasing demand for those

clothes and garments with high specifications and more performances, including easy-care garments (Kadolph & Langford, 2001; Schindler & Hauser, 2004).

Furthermore, flammability of textiles is a critical aspect to ensure the safety of consumers. Flame retardant finishes provide textiles with an important performance characteristic. Protection of consumers from unsafe apparel is one of the areas where flame retardancy is important. The demand for the flame retardant textiles is mainly in work clothing, military clothing, carpets and floor covering, upholstery and drapery. Flame retardant finishing is not carried out for normal adult apparel, but children's sleepwear is a promising market for the flame retardant textiles, especially cotton apparels (Weil & Levchik, 2008; Yang & Qiu, 2006; Schindler & Hauser, 2004). Cotton as a widely used textile fiber is a high flammable fiber, in which application of flame retardant products is important (Welch C. , 2001; Wu & Yang, 2006a). A commercially successful flame retardant textile product is needed to meet some important requirements: little or no adverse effect on physical properties of textiles, producing by a simple process with conventional equipment and inexpensive chemicals and durable to washing and laundering (Levin 1983; Schindler & Hauser, 2004). Most of the flame retardant finishing formulations were developed in period of 195-1970 (Wilkie & Morgan, 2010).

2.2 State of Research

2.2.1 Durable press finishing of cotton fabrics

2.2.1.1 Formaldehyde-based finishing agents

Crushing during use and care (like washing) cause wrinkles. Water absorption by cotton fibers leads to movement of the molecular chains of cellulose. The mobility of chains occurs in amorphous and intermediate (non-crystalline) regions. New arrangement of cellulose molecules is fixed by the hydrogen bonds between the adjacent hydrogen groups of the cellulose molecules (Lam et al. 2010). Thus, inhibiting the movement of cellulose chains is the appropriate way to overcome the problem. This goal is obtainable by crosslinking of the cellulose chains (Shahin et al. 2009; Lacasse & Baumann, 2004). The crosslinkers used for durable press finishing are also known as easy-care or durable press finishing agents.

The first group of easy care finishing agents was introduced at the end of 1920s. These products were N-methylol compounds, namely urea-formaldehyde or melamine-formaldehyde (Geubtner 1990; Berbner 1990; Wilder, et al. 1997). The action mechanism of these compounds was on the basis of N-methylol groups. The resulting N, N´-dimethylol urea reacted with methanol to form a more stable dimethoxymethyl urea (Figure 2.2.1). This product was highly reactive, has a low stability to hydrolysis and a high content of formaldehyde (Geubtner 1990; Schindler & Hauser, 2004).

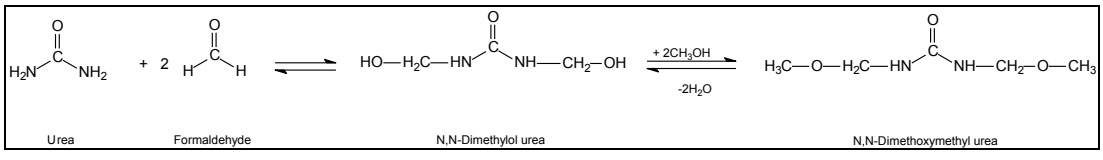

Figure 2.2.1 Dimethylol urea reactions

A crosslinking agent with more reactive groups lead to a better efficiency. Hence, melamine-formaldehyde with mostly three to six N-methylol groups could have higher crosslinking efficiency and better wash fastness. The synthesis of melamine-formaldehyde products was similar to urea-formaldehyde. Depending on molar ratio of reactants (melamine and formaldehyde) the product can be trimethylol melamine or hexamethylol melamine, which is finally modified to a methyl ether compound (trimethoxymethyl melamine and hexamethoxymethyl melamine, respectively-Figure 2.2.2) (Berbner 1990; Wilder, et al. 1997; Schindler & Hauser, 2004).

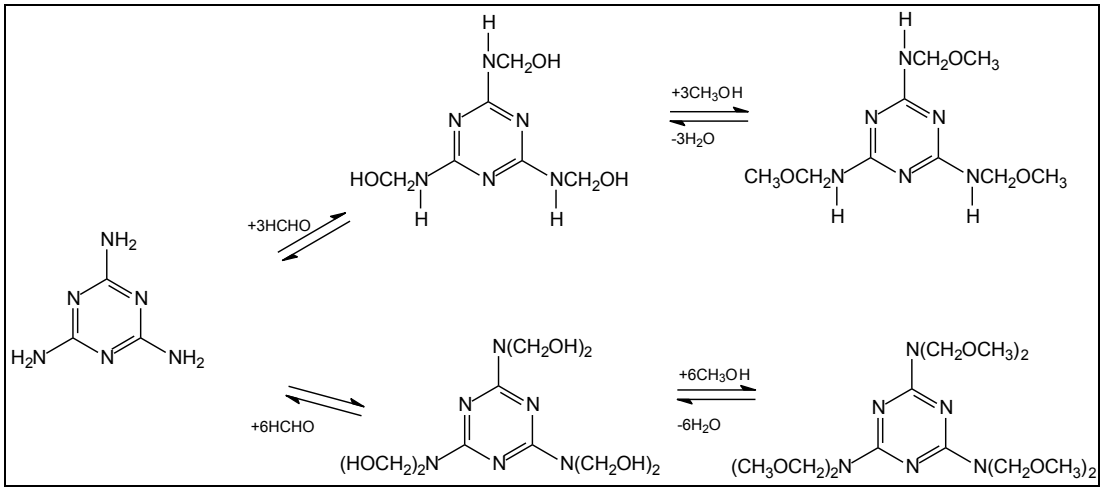

Figure 2.2.2 Reactions of melamine-formaldehyde

Better stability to hydrolyzing, better wash fastness and fewer problem with chlorine retention are the main advantages of melamine-formaldehyde products in comparison with urea-formaldehyde. Relatively high formaldehyde content and stiff handle of pretreated fabrics with melamine-formaldehyde are the known drawbacks of this product (Schindler & Hauser, 2004).

In 1947 dimethylolethylen urea products were used as the main easy-care finishing agents (Levin 1983; Sharpe & Mallinson, 2003). The main product in this group was N, N´-Dimethylol-4,5-dihydroxyethylen urea (DMDHEU).

DMDHEU was the final product of the reaction between urea, glyoxal and formaldehyde. The reaction of urea of glyoxal formed 4, 5-Dihydroxyethylene urea, which reacted with formaldehyde and formed DMDHEU (Schindler & Hauser, 2004; Chao & Somerville, 1973; Bezwada & Somerville, 1980). The synthesis of DMDHEU is shown in Figure 2.2.3.

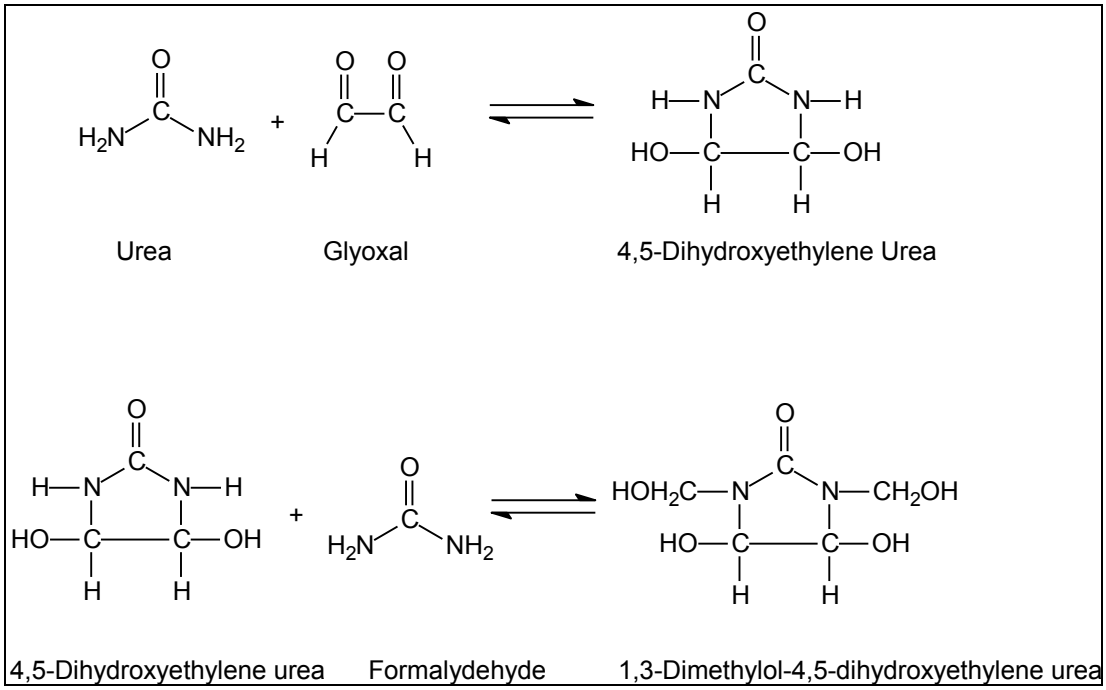

Figure 2.2.3 Synthesis of DMDHEU

The N-methylol groups in final DMDHEU can react with the hydroxyl groups of cellulose chains (Bajaj 2002; Andrews & Simoneaux, 1983; Vali & Arney 1971; Ibrahim et al. 2002). The mechanism of this reaction is shown in Figure 2.2.4.

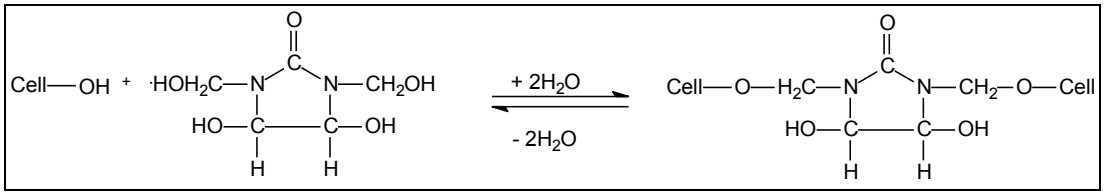

Figure 2.2.4 Crosslinking of cellulose with DMDHEU

By crosslinking of cellulose with DMDHEU, the movement of cellulose molecule chains is prevented and thus shrinkage and wrinkle formation in cotton fabric will be minimized. Preventing the movement of molecular chains in cellulose can also lead to loss of tensile strength. Crosslinking inhibits distribution of tear stress over many molecules, which can slightly shift the external forces (Schindler & Hauser, 2004). On the other hand, the acidic catalysts required in the chemical reactions of easy-care finishing of cotton fabrics can damage to the cellulose molecule. It can also be contributed to changes in the molecular chain length or degree of polymerization of cellulose molecules (Segal & Timpa, 1973). Excellent durability to laundering, low chlorine retention and medium to very low formaldehyde release are the main advantages of DMDHEU (Schindler & Hauser; 2004). Some researchers have tried to modify and improve some physical properties of application of DMDHEU. Wang and his colleagues employed alpha-amino acids (aspartic acids and glutamic acids) to join with DMDHEU and found that the combination of DMDHEU with the given alpha-amino acids can improve the wet crease recovery angel and the tensile strength retention (Wang et al. 2003).

2.2.1.2 Formaldehyde-free finishing agents

As Schindler and Hauser mentioned in their book of “chemical finishing of textiles”, use of formaldehyde makes several problems (Schindler & Hauser, 2004): formaldehyde can irritate mucous membranes, can cause teary eyes, cough and headache and make difficulties in breathing. Also skin contact with textiles that contain high levels of formaldehyde may lead to eczema and allergic reactions. Furthermore, formaldehyde is a suspected human carcinogen.

Due to the mentioned actual and specially the potential problems of formaldehyde release in DMDHEU-treated fabrics during production, storage and consumer use, since 1960s development of formaldehyde-free easy-care finishing agents, or chemicals that at least release less formaldehyde have been investigated (Brotherton et al. 1989; Choi & Welch, 1992; McKerron 1987; Yoon et al. 2003). Crosslinking of the cellulose molecular chains by use of formaldehyde was based on

the N-methylol reaction. Therefore, the early formaldehyde-free compounds were nitrogen-free finishes to avoid chlorine retention and hydrolysis, including aldehydes such as formaldehyde, glyoxal and glutaraldehyde (Frick & Harper, 1982; Choi & Kim, 2001; Yu et al. 2008; Lee & Kim, 2004). Formaldehyde itself if not a free-formaldehyde agent, has been considered as a low formaldehyde agent. Formaldehyde despite its good durable press performance causes a great loss in fabric strength and thus there is no more interest for this chemical (Frick & Harper, 1982). Glyoxal and glutaraldehyde (Figure 2.2.5) are reactive and in water form 4,5-dihydroxy-2-dihydroxymethyldioxalane and 2,6-dihydroxytetrahydropyran (Figure 2.2.6), which like formaldehyde cause more strength loss (in comparison to N-methylol compounds), yellowing of fabric, discoloring the fabric. Moreover, they are expensive (Frick & Harper, 1982; Whipple 1970; Whipple & Ruta, 1974; Kittinaovarat et al. 2006). However, to defeat the drawbacks of glyoxal and glutaraldehyde, the effect of some additives and catalysts has been studied. It has claimed that by using aluminum sulfate as catalyst and glycols as additive in the finishing bath of glyoxal, wrinkle recovery angle, tensile strength retention and whiteness index is improved (Lee & Kim, 2004). But aluminum sulfate is an expensive catalyst, too. Heretofore, Choi and Kim used sodium perborate and borax as additive in the finishing bath of cotton with glyoxal and glutaraldehyde (Choi & Kim, 2001). Their result showed an increase in whiteness index of the finished cotton by glyoxal and glutaraldehyde in the presence of perborate and borax, meanwhile the wrinkle recovery angle decreases. Yu, Lee and Bang suggested aluminum ammonium sulfate as a new catalyst, and diethylene glycol and polyurethane as additive for the glyoxal finishing system to minimize the decrease of physical properties of the finished cotton (Yu et al. 2008). The presence of aluminum ammonium sulfate improves the retention of tensile strength and whiteness, while diethylene glycol/polyurethane has no positive effect on the tensile strength and whiteness. Aluminum ammonium sulfate is also an expensive catalyst.

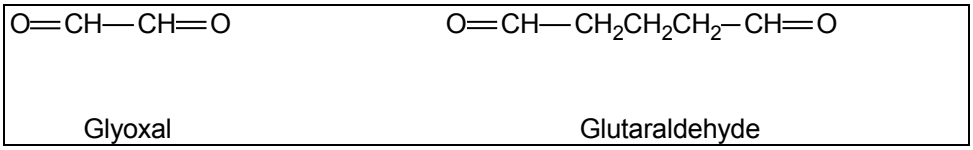

Figure 2.2.5 Glyoxal and glutaraldehyde

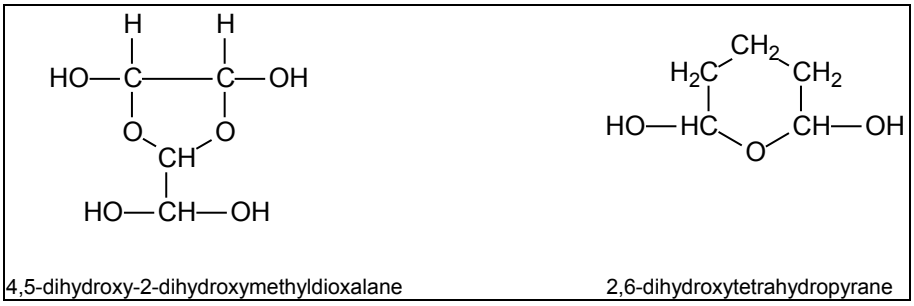

Figure 2.2.6 Cyclic hydrates of glyoxal and glutaraldehyde

Acetals have also been studied as nonformaldehyde crosslinking agents. Among them, the most effective are cyclic dehydrate hemiacetals, such as 2,5-dimethoxyfuran which is an succinaldehyde, 2,3-dihydroxy-1,1,4,4-tetramethoxybutane, 3,4-dihydroxy-2,5 dimethoxytetra-hydrofuran, and glyceraldehyde dimethylacetal. Acetals like formaldehyde cause more strength loss than methylolamide agents (Frick & Happer, 1984; Walker & Kokowicz, 1951; Chance et al. 1990).

Reaction products of amides and aldehydes have been considered as effective formaldehyde-free finishes. Among these products the reaction of urea and its derivatives (e.g. dihydroxyethyleneurea and dimethoxyethylenurea) with glyoxal has been extensively studied (Frick & Harper, 1982; Harper and Frick 1981; Gonzales & Benerito, 1965). The product of this reaction is N,N´-dimethyl-4,5-dihydroxyethxylen urea (DMeDHEU) or 4,5-dihydroxy-2-imidazolin (Figure 2.2.7). This compound is formaldehyde-free, has low chlorine retention and its effect as easy-care finishing agent is high enough (Schindler & Hauser, 2004). The

crosslinking reaction of DMeDHEU with cellulose is shown in Figure 2.2.8 (Schindler & Hauser, 2004).

However DMeDHEU has also a number of problems: it is expensive, it gives an acid-sensitive finish that can deteriorate without an afterwash, it does not give the level of wrinkle resistance given by methyloamides (Frick & Harper, 1982; Frick & Harper, 1981; Harper & Frick, 1981), limited durability to laundering and yellowing effect (Schindler & Hauser, 2004).

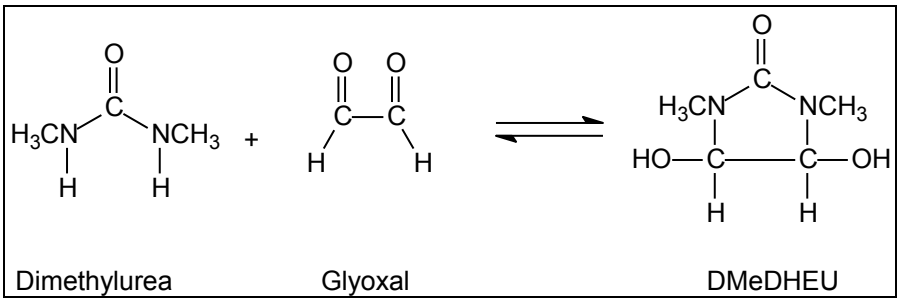

Figure 2.2.7 Synthesis of DMeDHEU

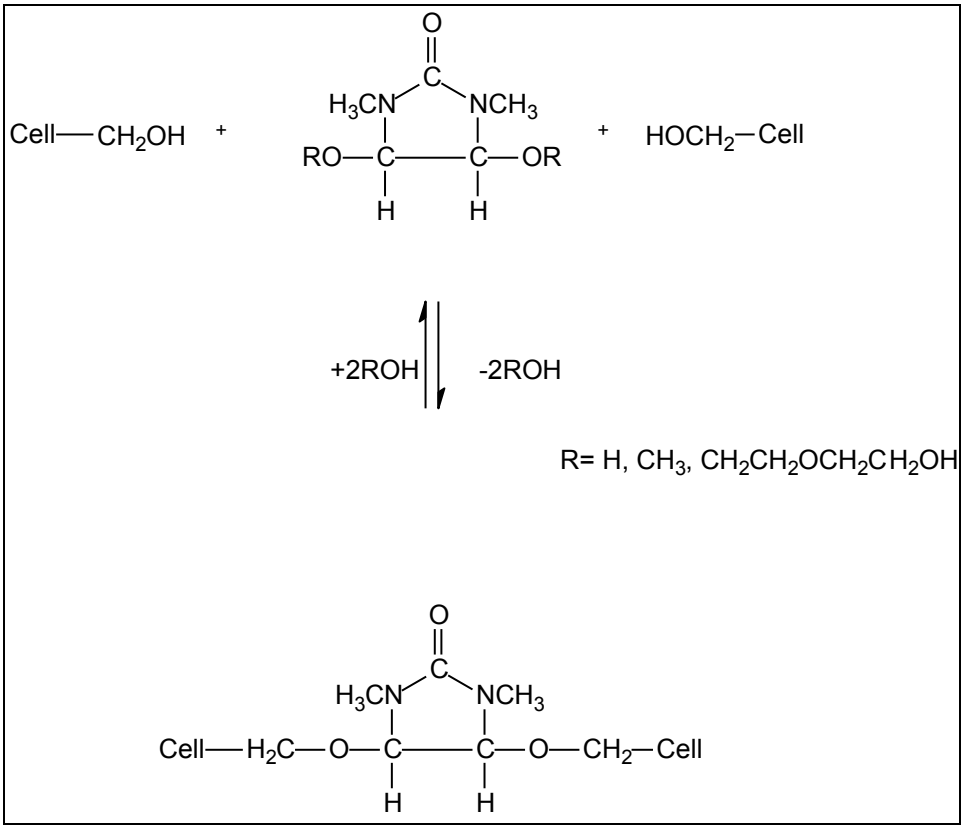

Figure 2.2.8 Crosslinking of DMeDHEU with cellulose

2.2.1.3 Polycarboxylic acids as formaldehyde-free finishing agents

Polycarboxylic acids are the most promising formaldehyde-free finishing agents (Andrews, 1990; Welch 1992; Welch, 1994; Welch, 1988; Welch & Andrews, 1989a).

Ester-crosslinking of cotton by polycarboxylic acids was firstly documented and published by Rowland and coworkers (Rowland, et al. 1967). In 1988, Welch reported the application of 1, 2, 3, 4-butanetetracarboxylic acid (BTCA) as an effective way to provide durable press cotton. BTCA imparts high levels of wrinkle resistance to cotton fabric (Welch, 1988; Welch & Andrews, 1989b). Since then, it has been tried to replace the formaldehyde-based chemicals with polycarboxylic acids. High quality crosslinking, high fabric strength retention and good durability against laundering are the advantages of finishing with polycarboxylic acids (Yang & Wang, 1996c; Yang & Kottes Andrews, 1991c; Welch & Andrews, 1989a; Welch, 1988; Yang, 1991a; Andrews et al. 1989).

1, 2, 3, 4 - butanetetracarboxylic acid (BTCA), citric acid (CA), succinic acid (SUA) and malic acid (MLA) (Figure 2.2.9) are the most conventional polycarboxylic acid as the durable press finishing agent (Welch, 2001; Yang et al. 1997b; Chen, Yang et al. 2005; Yang & Wang, 1996b; Yang & Wang, 1997a; Ibrahim et al. 2004). The effective polycarboxylic acids for durable press consist of at least three carboxylic groups which are able to form five or six-member cyclic anhydride rings. Except from BTCA, the other mentioned polycarboxylic acids have practically some drawbacks: citric acid causes yellowing of white cotton fabric, due to formation of α, β-unsaturated acids, i.e. cis-aconitic acid and trans-aconitic acid (Lu & Yang, 1999; Andrews & Trask-Morrell, 1991; Andrews et al. 1993; Yang et al. 1998). It usually needs the presence of other additives like nitrogenous additives (e.g. triethanoleamine hydrochloride) or glycol additives to be more activated (Ibrahim et al. 2002). Malic acid and succinic acid have been considered as a no effective crosslinking agent for durable press finishing of cotton fabric, since the presence of at least three carboxylic groups per molecule is necessary. Therefore, malic acid and succinic acid are usually applied with citric acid or BTCA together, or they can be

employed with a suitable catalyst like sodium hypophosphite, which wrinkle recovery angle will be improved. However, tensile strength reduced (Kim et al. 2000).

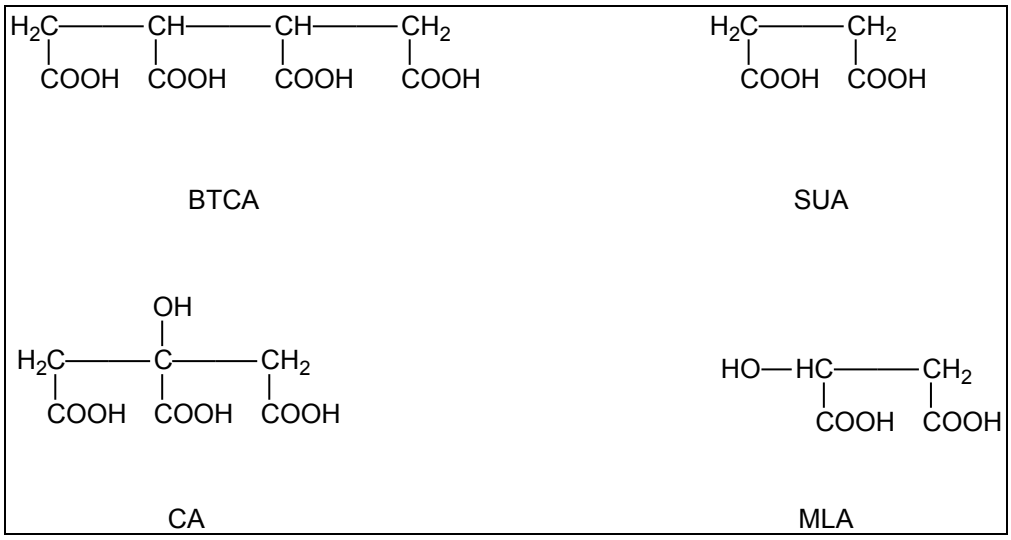

Figure 2.2.9 Conventional polycarboxylic acids for crosslinking of cotton

Polycarboxylic acids esterify the hydroxyl groups of cellulosic chains through the formation of cyclic anhydrides as reactive intermediate (Trask-Morrell et al. 1990; Welch, 1988; Welch, 1990). Yang and his colleagues examined formation of anhydride and ester in the treated cotton with different polycarboxylic acids using FTIR spectroscopy and measuring the absorbance of ester bond (Yang, 1991a; Yang & Kottes Andrews, 1991c; Yang, 1991b; Yang, 1993c; Yang, 1993a; Yang, 1993b; Yang & Bakshi, 1996a; Yang & Wang, 1996b). Yang also employed 17 different polycarboxylic acids to identify the formation of five membered cyclic anhydride intermediates (Yang & Wang, 1996b). He concluded that there are basically two steps in formation of the ester bonds: formation of a cyclic anhydride intermediate by dehydration of two carboxylic acids and the reaction between cellulose and the anhydride intermediate (Yang & Wang, 1996c; Yang, 1991b; Yang, 1993c; Yang & Wang, 1996b). This mechanism is summarized in Figure 2.2.10 (Yang & Wang, 1996c).

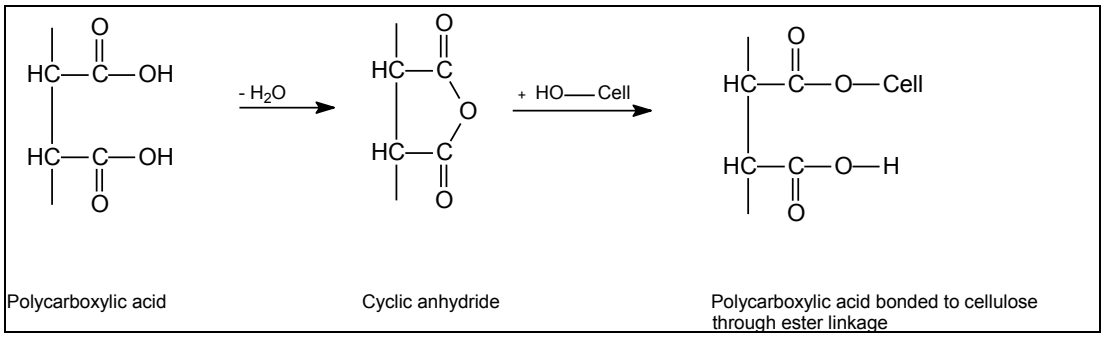

Figure 2.2.10 Esterification of cellulose with polycarboxylic acids through formation of cyclic anhydride

Among the studied polycarboxylic acids, BTCA is the most effective crosslinking agent (Yang & Wang, 1996b; Yoon et al. 2003; Kittinaovarat et al. 2006; Sauperl et al. 2009). The cyclic anhydride for BTCA will be in form of a dianhydride intermediate as shown in Figure 2.2.11 (Schindler & Hauser, 2004). Then the dianhydride intermediate of BTCA reacts with cotton cellulose (Figure 2.2.12).

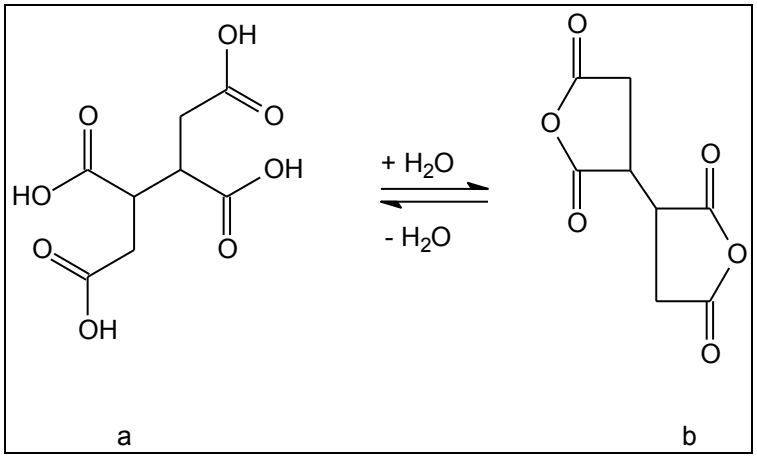

Figure 2.2.11 Formation of dianhydride intermediate in BTCA

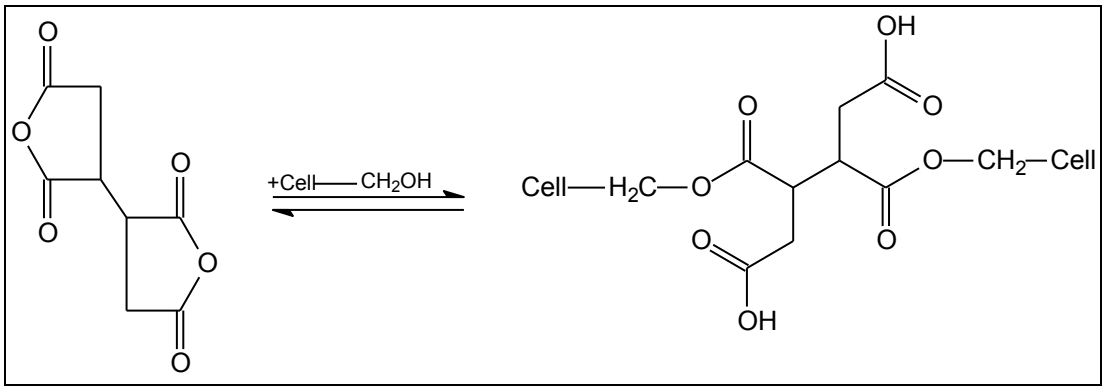

Figure 2.2.12 Crosslinking of cellulose with BTCA through dianhydride intermediate

The esterification reaction is accelerated, when a proper catalyst such as sodium hypophosphite (NaH_2PO_2) is employed. The other sodium salts of phosphoric acid have been also used: monosodium phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4) and trisodium phosphate (Na_3PO_4) (Brown & Tomasino, 1991; Andrews & Trask-Morrell, 1991; Trask-Morrell & Andrews, 1992; Welch, 1988; Welch & Andrews, 1989a). Also nonphosphorus catalysts have been investigated: aromatic N-heterocyclic compounds such as imidazole and its derivatives to improve the retention of mechanical properties of treated fabric (Choi et al 1993), base catalysts such as sodium carbonate and tertiary amines to minimize degradation of treated fabric and reduce the appropriate level of smooth drying appearance (Rowland, et al. 1967), and the other compound like mono- or disodium salts of α-hydroxy acids such as tartaric, malic, or citric acid (Rowland, et al. 1967). N-heterocyclic compounds are very expensive and base catalysts reduce the appropriate level of smooth drying appearance. The other mentioned catalysts are not as effective as sodium hypophosphite. Sodium hypophosphite is the best catalyst for crosslinking of cotton with polycarboxylic acids, especially BTCA. Because the highest levels of durable press rating and wrinkle recovery angle, reduction in cure temperature, increase of tensile strength retention and most satisfactory whiteness are obtained (Rowland, et al. 1967; Welch, 1988; Welch, 1990; Welch & Peter, 1997; Yang, 1993d; Morris et al. 1996; Yang, 2001; Lammermann 1992; Wei et al. 1999; Welch,

1992; Yang et al. 1998; Gu & Yang, 2000; Andrews & Trask-Morrell, 1991; Brown & Tomasino, 1991; Welch & Andrews, 1989b).

Nevertheless, BTCA has some limitations: high cost and requirement of large amount of sodium hypophosphite as catalyst, which is also not economically affordable and loss of mechanical strength (Lam et al. 2011; Bhattacharyy et al. 2003; Sircharussin et al. 2004; Schindler & Hauser, 2004). Recently some products based on polyacrylic acid, e.g. maleic acid and anhydride copolymers such as copolymers of maleic acid and itaconic acid and low molecular weight copolymers of maleic anhydride and vinyl acetate have been introduced and investigated. These compounds show good easy care performance and have more economical prices (Chen et al. 2005; Udomkichdecha et al. 2003; Yoon et al. 2003; Yang & Lu, 2000; Yang & Lu, 1999; Yang et al. 1998). Also the effect of co-catalysts in the finishing bath has been investigated, including: titanium dioxide (TiO_2) or nano-TiO_2 to enhance the finishing performance, improve the crease recovery angle and minimize the side effects (Lam et al. 2011; Yuen et al. 2007; Wang & Chen, 2005; Chen & Wang, 2006).

2.2.2 Flame retardant finishing of cotton fabrics

2.2.2.1 Mechanisms of flame retardants

Understanding of combustion process and flame progress is necessary to recognize the mechanism of flame retardancy in textiles. Combustion as an exothermic process requires heat, oxygen and a suitable fuel. Combustion is a self-catalyzing process which will continue until oxygen, heat or fuel is consumed (Schindler & Hauser, 2004). The whole process of burning is summarized in a simple diagram given in Figure 2.2.13 (Horrocks 1986).

By concerning the combustion process, it can be concluded that the mechanism of available flame retardants will be in one or more of the following ways (Horrocks 1986):

(a) removal of heat

(b) increasing the decomposition temperature, at which significant volatile gases form

(c) reducing the volatile and derived flammable gas formation and char promotion

(d) inhibiting the oxygen access to the flame

(e) increasing the ignition's temperature of the gaseous fuels, and/or interference with flame chemistry

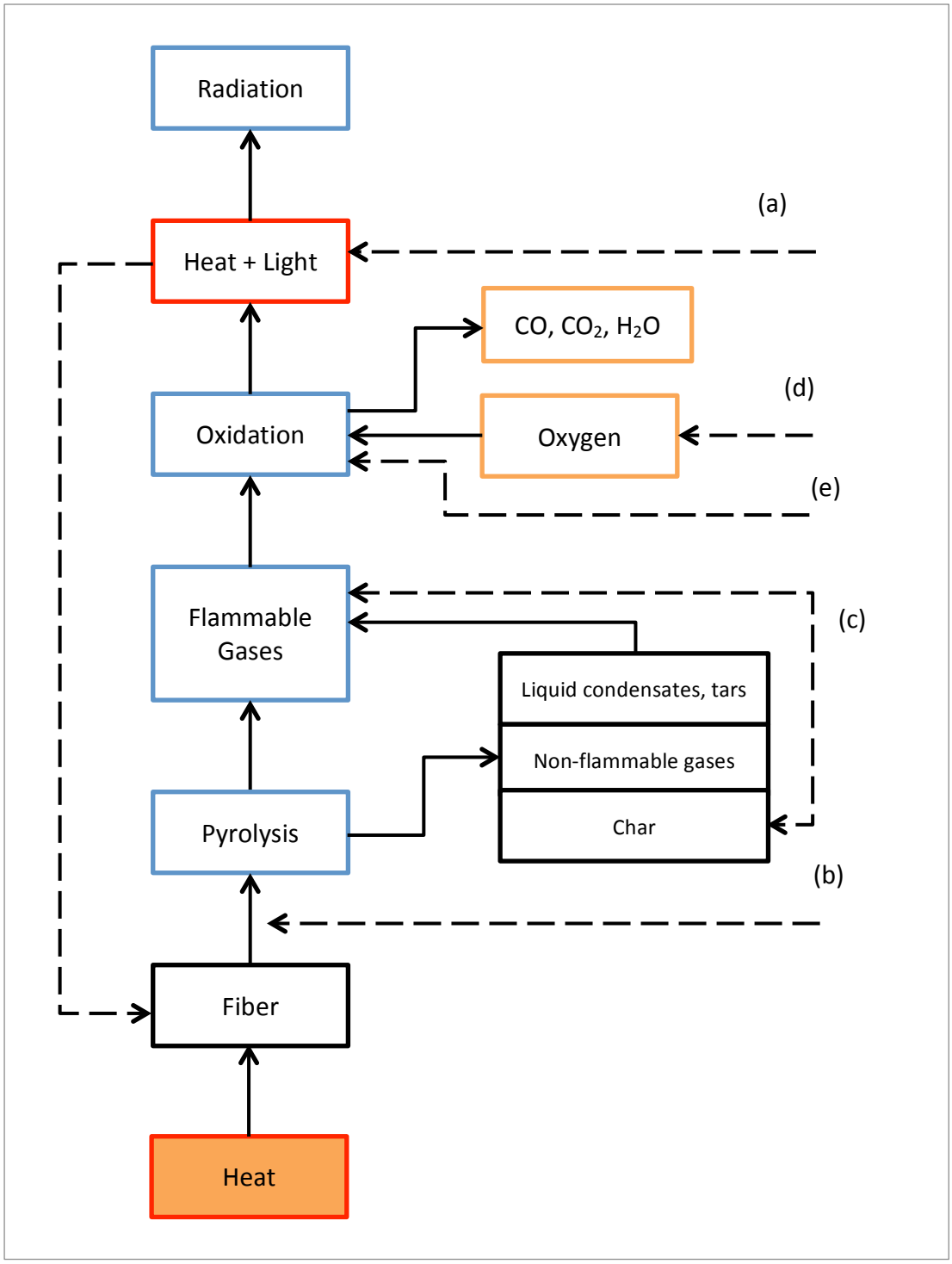

Figure 2.2.13 Combustion mechanism of fibers (Horrocks 1986)

Therefore, there are several practical methods to disturb the combustion cycle:

- using materials, which thermally decompose through endothermic reactions (Schindler & Hauser, 2004), such as aluminum hydroxide or aluminum trihydrate and calcium carbonate as coating (Horrocks & Price, 2000);

- using materials that are able to form an insulating layer around the fiber at temperatures below the pyrolysis temperature, such as boric acid and hydrated salts of boric acid. They release water vapor during heating and produce a foamed glassy surface on the fiber and consequently insulating the fiber from the oxygen and heat (Schindler & Hauser, 2004; Fahlman 2008);

- using phosphorus-containing materials, which produce less flammable volatiles and more residual char “condensed phase”, through producing phosphoric acid and its crosslinking with hydroxyl-containing polymers (Schindler & Hauser, 2004; Horrocks, 2003; Kandola et al. 1996)

- and interfere with free radical reactions “gas phase” by using halogen-containing materials, which yields hydrogen halides forming less reactive free radical and decreases the oxygen content through dilution of the flame gas (Schindler & Hauser, 2004; Horrocks & Price, 2000).

In case of the cellulosic fibers, formation of levoglucosan is the important thermal degradation mechanism. Levoglucosan and its volatile pyrolysis products are highly flammable materials and have the greatest share of the combustion in cellulosic fibers (see Figure 2.2.14). Flame retardants for cellulose are those compounds that can inhibit the formation of levoglucosan. Crosslinking and esterification of cellulose polymer chains with phosphoric acid reduce the formation of levoglucosan, catalyzes the dehydration and carbonation of cellulose and thus acts as an effective flame retardant mechanism. The most effective durable flame

retardant for cellulose are based on the phosphorus-and nitrogen containing chemicals, which can react with the fiber or build crosslinks in the fiber structure. Formation of phosphoric acids during the early stages of the fiber pyrolysis catalyze the dehydration reaction of cellulose and yield char at the expense of volatiles formation reactions are the most successful flame retardants of cellulose. However, presence of nitrogen also plays a significant role through providing a synergistic effect with phosphorus (Schindler & Hauser, 2004; Horrocks, 1986; Horrocks, 2003; Horrocks, 1983).

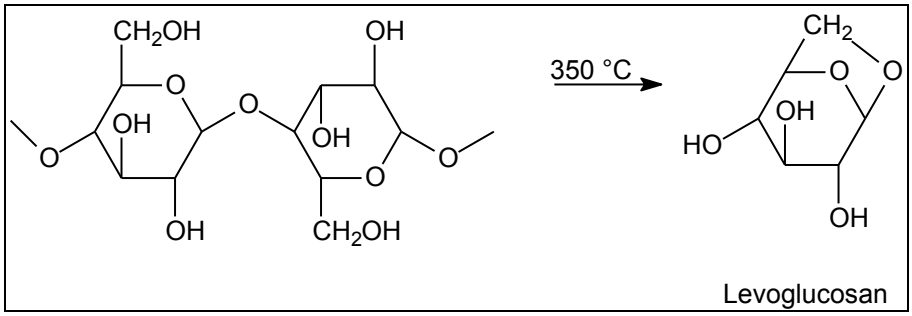

Figure 2.2.14 Thermal degradation of cellulose

2.2.2.2 Non-durable and semi-durable flame retardants

Non-durable flame retardants are those materials that are not expected to expose water, perspiration or rain and will wash readily with plain water. The flame retardants which are somehow resistant against water soaking or leaching but generally not against laundry washing or a few laundering are categorized as semi-durable flame-retardants (Schindler & Hauser, 2004; Weil & Levchik, 2008). Ammonium sulfate and the mixture of boric acid and borax are effective non-durable flame retardants for cotton fibers. Also ammonium salts of strong acids, especially phosphoric acid (due to the synergistic effect of nitrogen and phosphor) are useful compounds. Mono- or diammonium phosphate, ammonium sulfamate and ammonium bromide are the known commercial products. Water-soluble low molecular weight ammonium polyphosphate (see Figure 2.2.15) is also used. It can be a semi-durable flame retardant depending on the degree of polymerization. The

high molecular weight water-insoluble ammonium polyphosphate can be used with a melamine-formaldehyde resin coating and also with glass microspheres. Ammonium bromide and its combination with ammonium phosphate provide an effective non-durable flame retardant in the gas phase (Schindler & Hauser, 2004, Weil & Levchik, 2008; Wilkie & Morgan, 2010; Kandola et al. 1996; Horrocks & Price, 2000; Vorman et al. 2004).

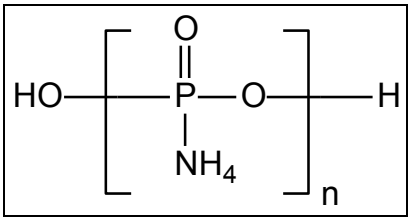

Figure 2.2.15 Ammonium polyphosphate
(Horrocks & Price, 2000)

Combination of ammonium polyphosphate and urea can improve the durability of flame retardancy against washing. The semi-durable flame retardants are not durable against alkaline laundering, because alkaline conditions can cleavage cations to acid hydrogen or ammonium. By use of organic phosphoric acid, such as $CH_3PO(OH)_2$ instead of phosphoric acid, the obtained finish will have less sodium ion-exchange. Thus, a suitable nitrogen-based compound will be cyanoguanidine, such as Flavon® CGN-Ciba, which is a cyanoguanidine salt of methylphosphinic acid. The combination of cyanoguanidine with boric acid and urea is even more effective and more durable (Weil & Levchik, 2008; Dermeik et al. 2006). Backcoating with phosphorus-containing formulation is the another approach to provide semi-durable flame retardants. Horrocks showed that using ammonium polyphosphates optionally combined with additional char formers, such as pentaerythritol are effective backcoating for cellulosic fibers (Horrocks, 1996). For more resistance to hot water, coated ammonium polyphosphate, such as Exolit® AP-462 or Budenheim's FR CROS® 487 and coated melamine-formaldehyde resin, such as Budenheim's FR CROS® 489 may be used (Weil & Levchik, 2008). Phosphorus-

containing coatings form a barrier of foamed char, when the textile is exposed to fire, such as ammonium polyphosphate-pentaerthyritol-melamine-binder formulation. The binder can be acrylic compounds such as vinylidene chloride/acrylic latex (Weil & Levchik, 2008; Cox 2005; Kandola & Horrocks, 2000; Dombrowski 2002).

2.2.2.3 Durable flame retardants

The most successful and effective durable flame retardant systems of cellulosic textile are based on phosphorus and nitrogen containing compounds. They can react with the fiber or from crosslinks on the fiber, based on formation of char and preventing the formation of undesirable levoglucosan and flammable volatiles (Schindler & Hauser, 2004; Gaan & Sun, 2009; Horrocks, 1983). The most important commercial product with more than 50 years history and still exposed to improvements, is tetrakis (hydroxymethyl)phosphonium chloride) (THPC). It is a reactive product from the addition of formaldehyde to phosphine. THPC reacts with urea forming an insoluble crosslinking net on cellulose by a pad-dry-cure process (Weil & Levchik, 2008; Schindler & Hauser, 2004; Frank et al. 1982; Benitate & Harper, 1987; Lecoeur et al. 2001; Wu & Yang, 2007a; Gaan & Sun, 2007a). The synthesis of THPC and its reaction with urea are shown in Figure 2.2.16 and Figure 2.2.17, respectively.

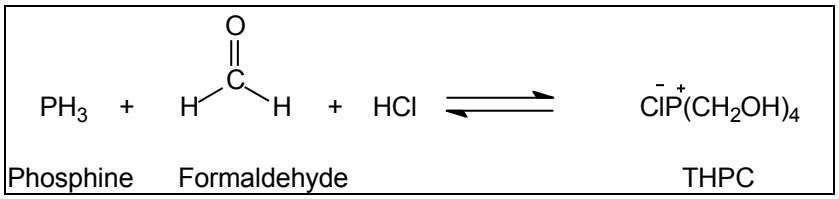

Figure 2.2.16 Synthesis of THPC

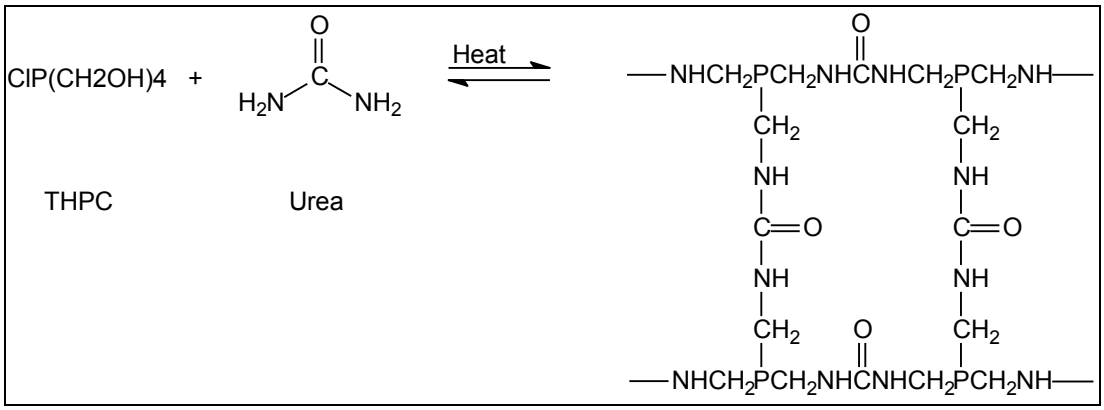

Figure 2.2.17 Reaction of THPC with urea

Despite highly effective and durable flame retardancy of THPC-urea system in cellulosic textiles, treated fabric becomes stiff and tensile strength is reduced. Moreover, formaldehyde release is an important disadvantage of this flame retardant (Schindler & Hauser, 2004). To solve these problems, a variation on THPC-urea system has been developed. This variation, as the most commercially successful approach (Weil & Levchik, 2008) is known as Proban® process (Cole, 1978). It is based on a careful reaction of THPC with urea, which the resulted precondensate is padded onto cotton at pH 5-8. Then fabric is exposed to ammonia vapors followed by oxidation with peroxide (Schindler & Hauser, 2004; Weil & Levchik, 2008; Horrocks, 1986). Fig 2.2.18 shows this mechanism. The final finishing product provides a very good durable retardancy with better improved fabric physical properties (Levin, 1983).

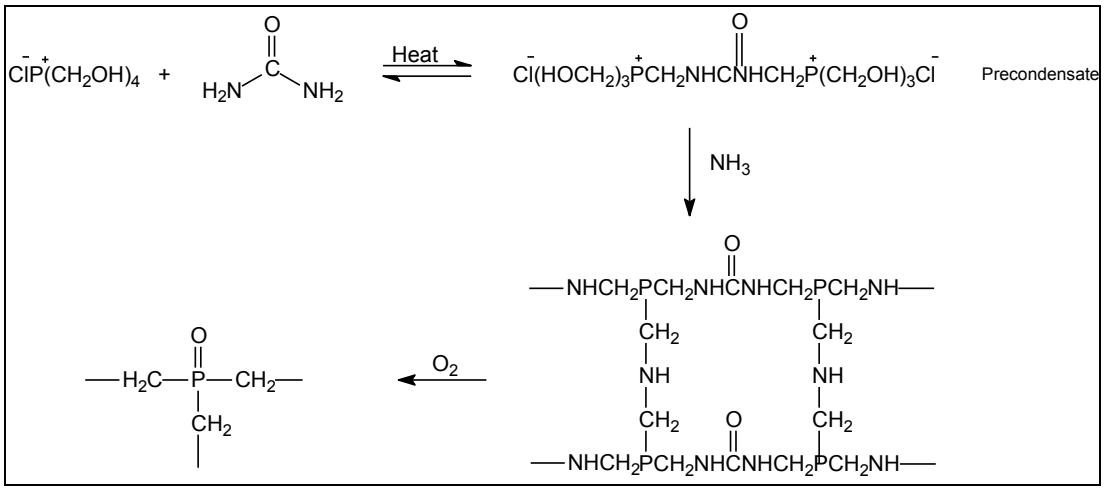

Figure 2.2.18 THPC-urea-ammonia reaction

The other successful commercial durable flame retardant is a well-known product, Pyrovatex CP (Weil & Levchik 2008; Kandola et al. 1996; Horrocks, 1986; Horrocks, 2003; Weil, 1992). Pyrovatex CP is N-methylol dimethyl phosphonopropionamide and applied with a methylolated melamine (e.g. trimethylol amine) resin in the presence of phosphoric acid. It catalyzes the formation of pyrovatex-resin-cellulose moieties through hydroxyl group of C6 (Weil & Levchik 2008; Hebeish et al. 1994). Also the presence of methylolated melamine can improve the flame retardancy of the whole system by phosphorus-nitrogen synergism (Yang et al. 2005). The mechanism is shown in Figure 2.2.19.

Also a flame retardant finishing system was developed for cotton and cotton blends based on the combination of hydroxyl-functional organophosohorus oligomers and a bonding agent, such as methylol amines compounds (e.g. DMDHEU and trimethylolmelamine). It makes a durable flame retardant system with little change in fabric whiteness and tensile strength (Yang & Yang, 2003; Wu & Yang, 2004; Yang et al. 2005; Wu & Yang, 2006b; Wu & Yang, 2007b; Yang & Qiu, 2006).

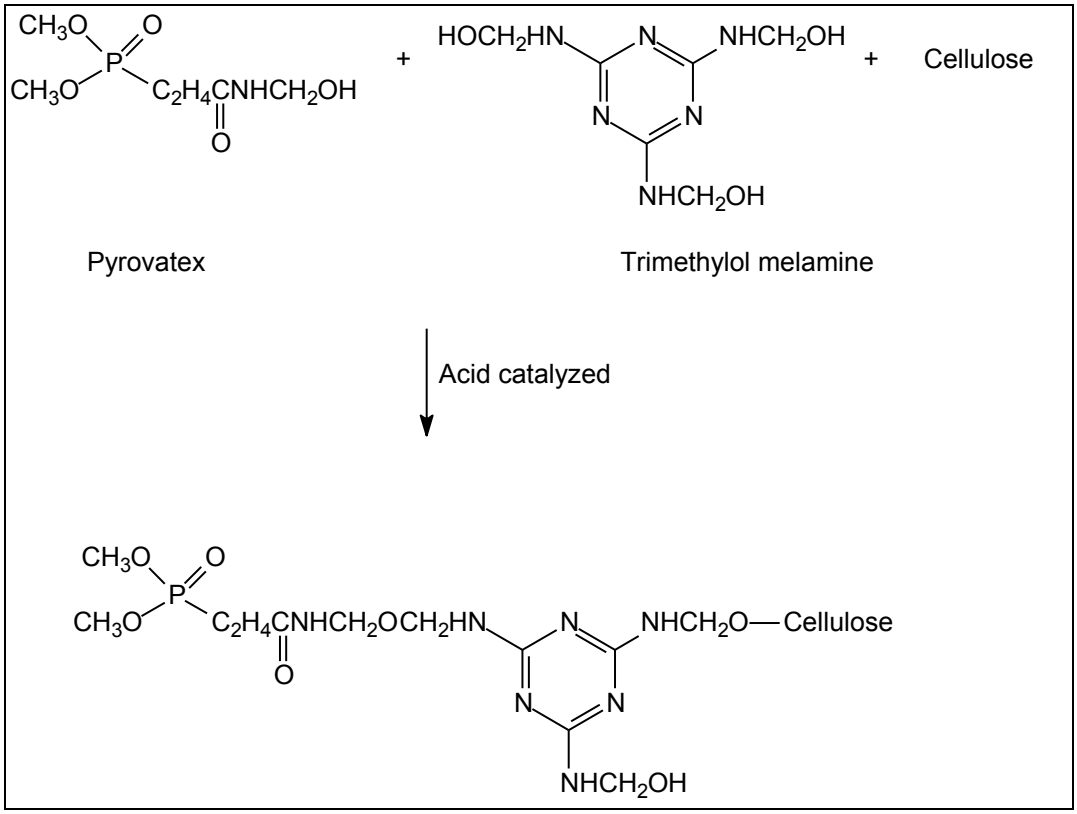

Figure 2.2.19 Reaction of Pyrovatex CP with cellulose in presence of trimethylol amine

The problems of formaldehyde release in these products despite their successful performance in flame retardancy of cotton fabrics led to investigate formaldehyde-free flame retardants. Application of polycarboxylic acids as flame retardants of cotton and cotton/polyester carpets was firstly reported by Blanchard and Graves (Blanchard & Graves, 2002). They reported that phosphorus-containing oligomes of maleic acid reduces flammability and increases char formation of cotton/polyester fleece (Blanchard & Graves, 2005). Wu and Yang have investigated unsaturated bifunctional acid (maleic acid) and a phosphorus-containing inorganic compound (sodium hypophosphite) to reduce the flammabilty of cotton fleece, in which durable flame retardancy and easy-care properties in cotton fleece with low cost and were obtained (Wu & Yang, 2008). Also the other polycarboxylic acids, such as succinic acid, malic acid, tartaric acid, citric acid and 1, 2, 3, 4-butanetetracarboxylic acid have been applied. These polycarboxylic acids in the presence of sodium hypophosphite are able to reduce the flammability of cotton

fabrics (Wu & Yang, 2009; Cheng & Yang, 2009a; Cheng & Yang, 2009b; Wu et al. 2010).

2.3 Aim of study

The goal of this part of study is development and application of new formaldehyde-free crosslinkers for multifunctional finishing of woven cotton fabrics using novel polycarboxylic acids and reducing the practical drawbacks of conventional polycarboxylic such as deterioration of physical and mechanical properties of treated fabrics (whiteness index, tensile strength and washing fastness). These requirements can be realized by carboxylation of commercially available polyvinylamines, polyethyleneimines and other polyamines and their derivatives, which forms of a polyamino/polyimino carboxylic acid. These new compounds in comparison to the conventional polycarboxylic acids have a large amount of functional carboxylic groups. The presence of free amino groups in partially carboxylated polyamines/polyimines provides further reactions to obtain more functional effects. Based on the chemical structure of carboxylated polyamines as the derivative of polyamines the finished fabric will be resistant to wrinkling (durable press effect), resistant to flammability (flame retardant) and also resistant to growth of microorganisms and bacteria (biostatic and antibacterial). Thus, the final product of this finishing system is a cotton fabric with multifunctional performance by use of a single finishing process, which helps to reduce and optimize the energy consumption, time and costs of process.

2.4 Basic approaches

Polycarboxylic acids are relatively new generation of durable press finishing agents for cotton fabrics. In comparison to the conventional formaldehyde-based easy-care agents (e.g. DMDHEU) polycarboxylic acids contain no formaldehyde and thus more environmental friendly. However, polycarboxylic acids cause yellowing of fabric and decrease tensile strength. Moreover, they are expensive. On the other hand, combination of polycarboxylic acids with sodium hypophosphite has flame retardancy effect on cotton fabrics. But they are not normally used as flame retardant for cotton fabrics, because they can just reduce the flammability of cotton and cannot prevent it.

In this regard, polyamines may be interesting compounds. The presence of a large number of amino functional groups in these molecules makes further reactions and applications possible. Polyvinylamine and polyethyleneimine are two well-known polyamines that are already produced on an industrial scale for various industrial applications. Polyvinylamine (PVAm) is a linear cationic polymer with the chemical structure shown in Figure 2.4.1a (Schröder, 1994). There are primary amino groups in the molecular chain of this polymer, which can be easily functionalized (Imamura et al. 2003; Renz et al. 1997). Polyethylenimine (PEIm) is a branched polymeric amine with primary, secondary and tertiary amino groups, as shown in Figure 2.4.1b.

Protonated polyvinylamines and polyethyleneimines have a high charge density and can be adsorbed to the negative charged surfaces. The industrial applications of polyamines can be enlarged through chemical modification of these compounds.

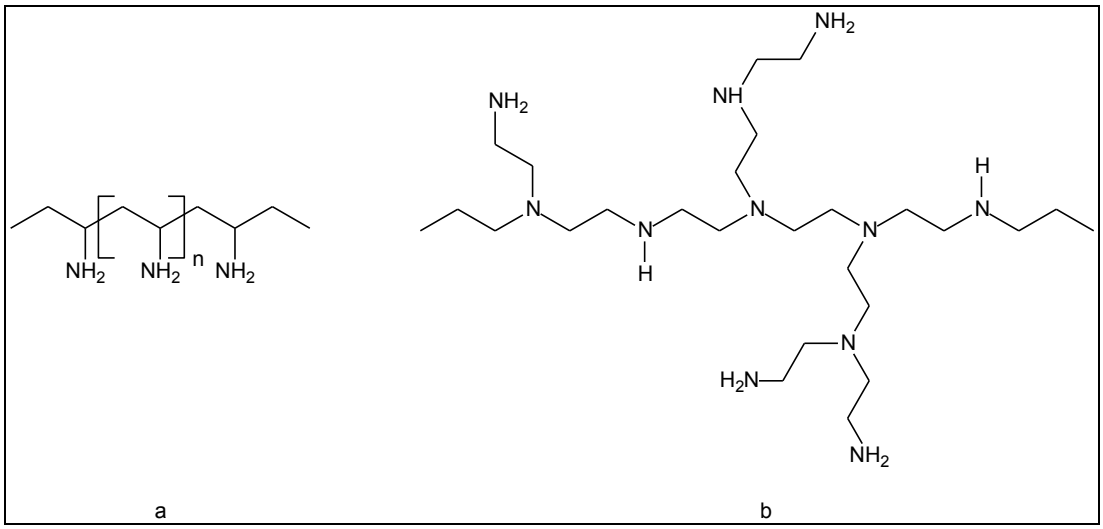

Figure 2.4.1 Chemical structure of polyvinylamine (a) and polyethylenimine (b)

For example, pigment dispersants for non-polar solvents are obtained by amidation with fatty acids. Through an alkoxylation of polyethyleneimine the number of primary and secondary amino groups will be decreased, while compatibility with anionic compounds in the formulations is improved. Carboxylation of polyamines leads to formation of amphoteric polymers with excellent complexing-properties. These derivatives also possess dispersant properties, e.g. polyvinylamine is used in paper and pulp industry to remove particles. It also serves to increase the wet and dry strength of paper (Auhorn, 1999; Übenacker et al. 2002; Thölmann et al. 2003). Primary amino groups in the polymer chain of the polyvinylamine and corresponding co-polymers can be functionalized. Some reactions with typical electrophiles such as epoxides, anhydrides, isocyanates, etc., are known and schematically shown in Figure 2.4.2 (Renz et al. 1997; BASF, 2004).

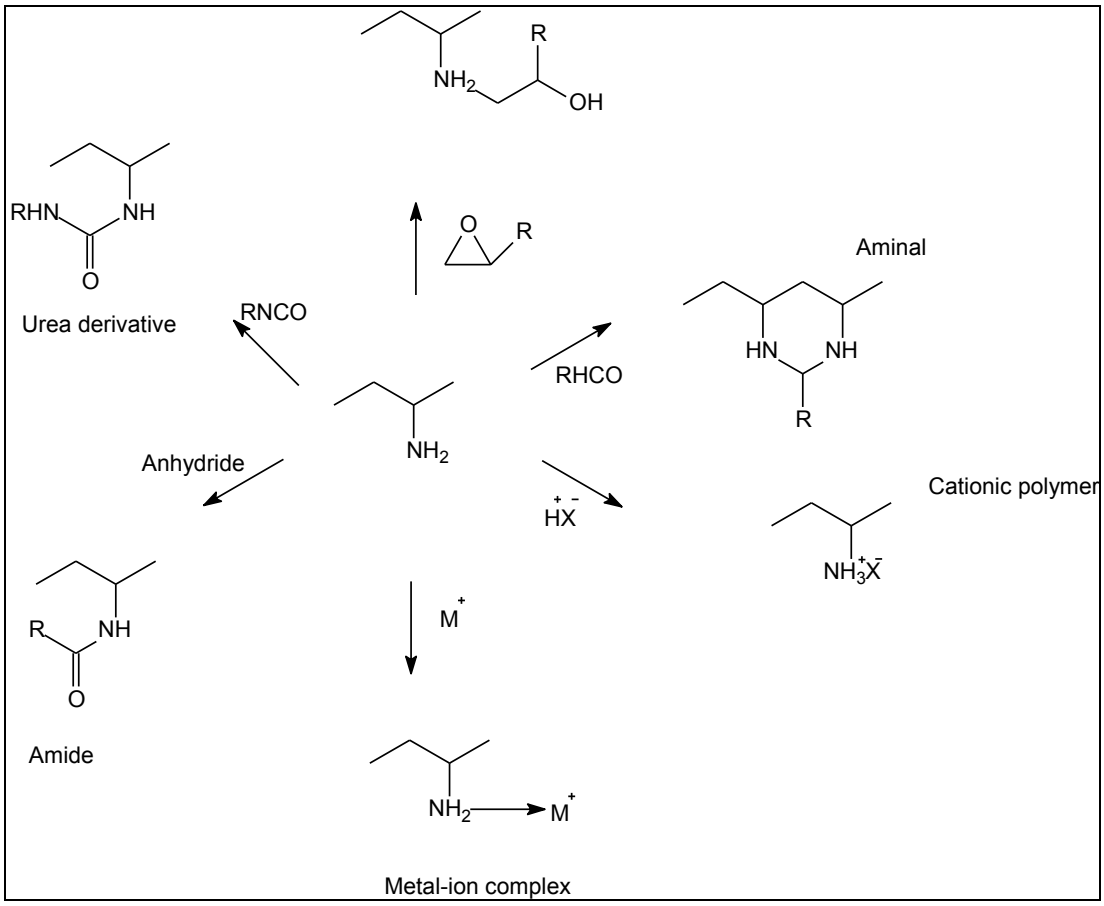

Figure 2.4.2 Selected possible reactions of polyvinylamine (BASF 2004)

Since polyvinylamine and polyethyleneimine are produced in industrial scale and in large quantities, they can be principally used as starting compounds for the new durable press finishing agents of cellulosic materials. These chemical products are ideal for textile industry and also for the aim of this study, because they are not toxic and they pose no human hazard potential. For use in the textile finishing industry is also important that these compounds are not hazardous for water. Therefore, as a starting material for finishing products of cotton textiles, polyethyleneimine and polyvinylamine can be used.

Via a reaction with halocarboxylic acids, such as bromoacetate ($BrCH_2COOH$), under basic conditions, the hydrogen atoms at the primary amino groups of polyethylenimine and polyvinylamine can be replaced by carboxyl groups (Figure 2.4.3).

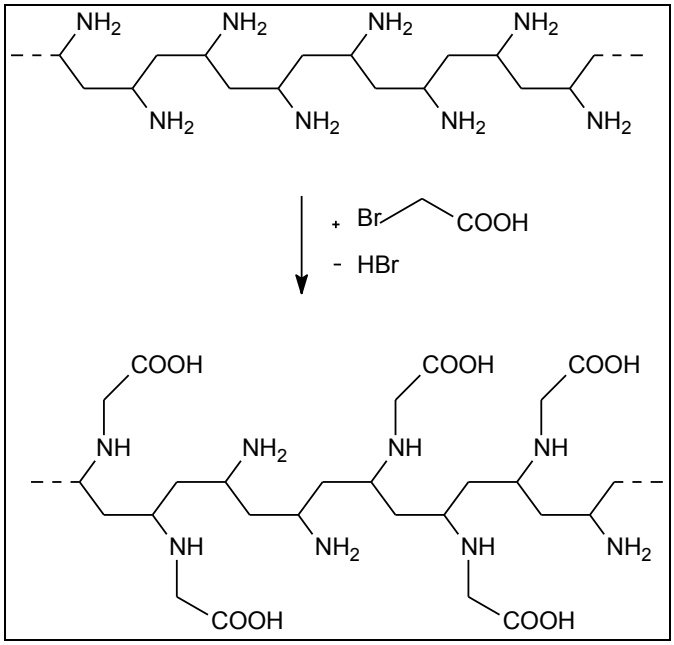

Figure 2.4.3 Synthesis of polyamino carboxylic acid via reaction of PVAm with bromoacetic acid

The carboxylated polyvinylamine (polyamino carboxylic acid) reacts with the hydroxyl groups of cotton cellulose (Figure 2.4.4). The same reaction is possible for the carboxylated polyethylenimine.

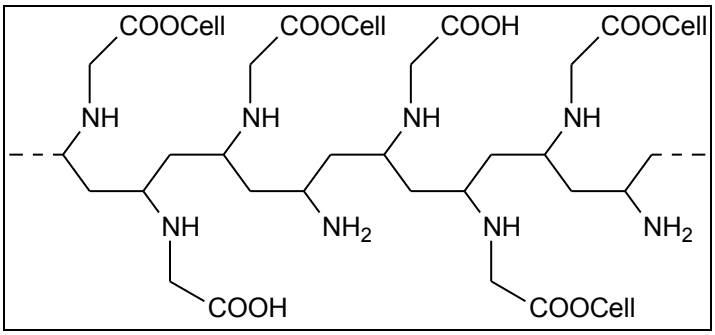

Figure 2.4.4 Crosslinking of cotton with carboxylated polyvinylamine (polyamino carboxylic acid)

Partially carboxylation of polyvinylamine or polyethyleneimine provides further reactions and thus more effects on the fabric (Figure 2.4.5).

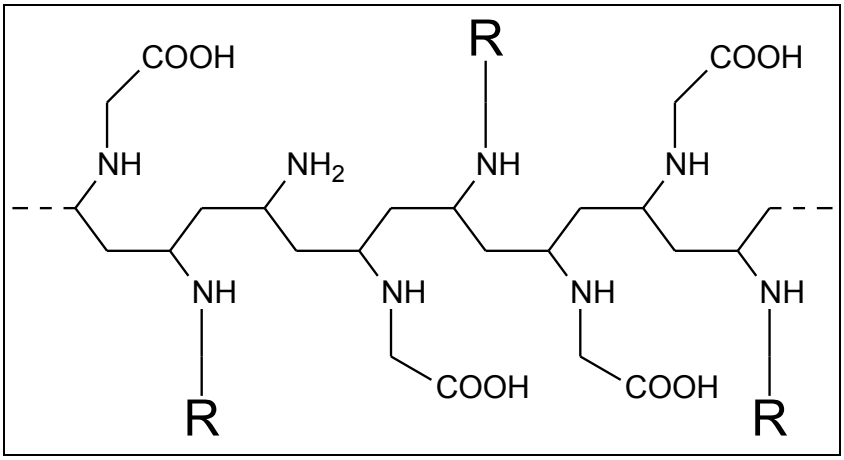

Figure 2.4.5 partially carboxylate polyvinylamine with further substitution (R)

(R= fluorinated alkyl chains, hydrophobic residues, hydrophilic residues, any functional groups)

In detail, the solutions to achieve the research objectives are summarized as follows:

1. Chemical characterization of the carboxylated polyamines

2. Investigating the various suitable halocarboxylic acids for carboxylation of polyamines

3. Determination of the optimal process parameters

4. Evaluating the finishing affects, including wrinkle recovery angle, tensile strength, whiteness index and wash fastness

5. Determining the biostatic properties of the finished fabric

6. Studies on the flammability of finished fabric

7. Investigating the dyeability of finished fabric with reactive dyes

2.5 Materials and methods

2.5.1 Materials

A standard scoured, bleached and desized plain woven cotton fabric (density 110.66 g/m2) was supplied by Testex. Polyvinylamine (Lupamin 1595®, Mw 10000 g/mole, concentration 10-15%, BASF), bromoacetic acid (99%, Merck), 3-bromo-propionic acid (Alfa-Aesar), hydrochloric acid (32%, Merck), ethanol (Merck), sodium hydroxide (99%, Merck), acetic acid (99%, Merck), phosphoric acid (85%, Merck), boric acid (Flucka), methylene blue (Merck), potassium bromide (Merck), sodium hypophosphite (Alfa Aesar), and a cation exchanger (Lewatit SC 102, Bayer AG) were used as commercial products without any further purification.

The reactive dyes Remazol Red RB, Remazol Yellow 3RS and Remazol Brilliant Blue BB used for dyeing of cotton were purchased from DyeStar GmbH & Co.

2.5.2 Methods

2.5.2.1 Carboxylation of polyvinylamine (PVAm)

Polyvinylamine (PVAm) was carboxylated by adding bromoacetic acid to an alkali aqueous solutions of PVAm (1 – 8% w/v, pH 11, different mole ratio PVAm:bromoacetic acid; 1.00 : 0.25, 1.00 : 0.50, 1.00 : 0.75 and 1.00 : 1.00). The reaction was completed after 24 h at room temperature and the pH value of the solution was adjusted to 6-7 using hydrochloric acid. Water was removed under vacuum and the obtained solid was washed with ethanol. A cation exchanger (20 g in 200 ml distilled water) was used to extract sodium chloride and sodium bromide from the solid. The solution was evaporated under vacuum and the resulted solid washed with ethanol and dried at 60 °C for 24 hours.

2.5.2.2 Chemical characterization of carboxylated PVAm

The degree of substitution (DS) was calculated from elemental analysis using the ratio of carbon to nitrogen (C/N) of the carboxylated PVAm. FTIR and ^{1}H-NMR

spectroscopy were used for further characterization of the carboxylated PVAm. FTIR spectroscopy was carried out by an IRPrestige-21 (Shimadzu) with resolution of 4 cm^{-1} and 40 scans for each spectrum. Potassium bromide was used as reference material. The elemental analysis of the synthetized carboxylated PVAm was done by EA 3000 (Hekatech). ^{1}H-NMR spectra was recorded using a Bruker DMX300 with deuterated ethanol as solvent.

2.5.2.3 Finishing of cotton with carboxylated PVAm

Finishing of cotton samples was done by a pad-dry-cure process. Each cotton sample weighted 8 g and the liquor-to-goods-ratio was 12.5 : 1. The cotton fabrics were stirred for 2h at room temperature in the solutions containing carboxylated PVAm (1% w/v) and sodium hypophosphite (60 g/l) as catalyst. Afterward, they were padded in a laboratory padding frame with 100% wet pick-up, dried at 85 ^{o}C for 10 min and cured at 170 ^{o}C for 6 min in a Matthis stenter. Finally the finished cotton fabrics were rinsed for 5 min with tap water and then 5 min with distilled water to remove unreacted chemicals from the surface of the cotton fabrics. The rinsed samples were dried at room temperature and conditioned (24 h, 20 °C, 65% humidity).

2.5.2.4 Gravimetric test

The gravimetric test was based on increased weight of conditioned samples (24h – 20 °C – 65%) humidity before and after finishing with carboxylated PVAm, according to the following equation:

$$\text{Relative weight increase (\%)} = \frac{m_2 - m_1}{m_1} \times 100$$

Equation 2 Relative weight increase

Where m_1 is the weight of original sample and m_2 is the weight of sample after finishing with polycarboxylic acid. Every experiment was performed in triplicate. The precision of the obtained value of relative weight increase was ± 1.2 %.

2.5.2.5 FTIR spectroscopy of finished cotton fabric

An IRPrestige-21 (Shimadzu) was used for study of FTIR spectroscopy of the finished cotton with resolution of 4 cm-1 and 40 scans for each spectrum. The samples were treated with 0.1 M NaOH solution at room temperature to convert the free carboxyl to carboxylate, dried and finally prepared by pressed-disc technique before FTIR spectroscopy (Yang C., 1991b; Lewis & Voncina, 1997a; Lewis & Voncina, 1997b; Udomkichdecha et al. 2003).

2.5.2.6 Determination of carboxylic groups in finished cotton with carboxylated PVAm

Dyeing with cationic dyes can be used for quantitatively measuring of carboxyl groups in cotton fabric. According to principals of ion-exchange, cationic dye methylene blue can be attached to the negatively charged carboxyl groups. Thus this treatment should be carried out in an alkaline medium (pH 7.2). After completion of dyeing, attached cationic dye can be again extracted through an acid-treatment (Figure 2.5.1). From the extracted cationic dye, the original amount of attached dye can be measured by UV-VIS-spectroscopy and then the amount of available carboxyl groups (free carboxylic groups on the cotton fabric) will be calculated (Klemm et al. 1998). To prepare the alkaline medium, Britton-Robinson buffer solution was employed, which contained 2.29 ml/l acetic acid (99%), 2.70 ml/l phosphoric acid (85%), 2.47 g/l boric acid and 550 ml/l sodium hydroxide (0.2 m) and pH adjusted at 7.2 (Britton & Robinson, 1931). Then each sample was dyed in a 0.05 % solution of methylene blue in Britton-Robinson buffer solution, stirred 10 min in room temperature, rinsed thoroughly with distilled water and dried at room temperature. Each dried sample was weighed and stirred for 1h in 20 ml solution of acetic acid (84%) until the samples became discolored. Afterward, the

amount of extracted methylene blue was spectroscopically measured in Cary5E (Varian) at wavelength of maximum adsorption.

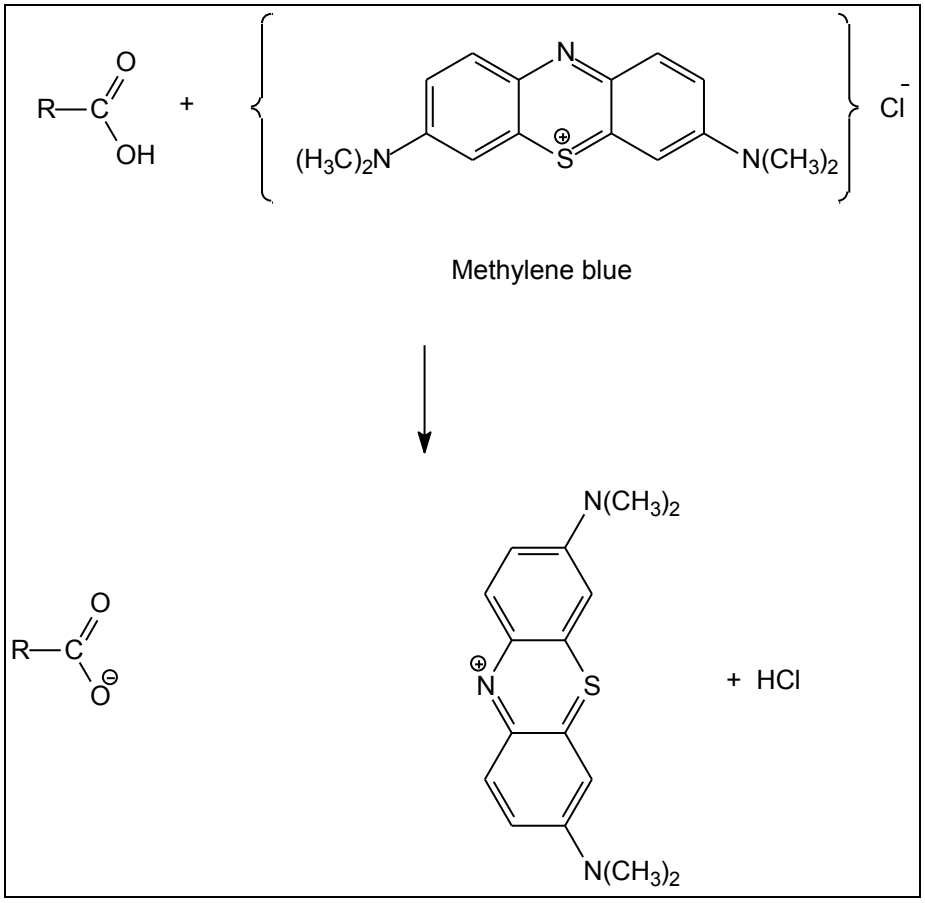

Figure 2.5.1 Mechanism of methylene blue test for quantitative determination of carboxylic groups in cotton samples

2.5.2.7 Measurement of free amino groups in treated cotton

To protonate the free amino groups, the finished cotton samples were immersed in dilute hydrochloric acid (pH 4-5) for a few minutes and afterward washed with distilled water to remove hydrochloric acid. Then, the samples were dried at room temperature, afterward at 100 ° C for 1 hour, conditioned, and accurately weighed. These samples were mixed with 25 ml water and titrated with 0.02 m sodium hydroxide. The addition of sodium hydroxide was carried out in 0.10 ml increments. The pH of the solutions was measured with a pH electrode, based on the measured value of the stable potential.

2.5.2.8 Dyeing with reactive dyes

All dyeing were carried out in a textile linitester with a liquor ratio 50:1, 2% o.w.f.[1] depth of dyeing and the weight of samples was 1 g. The cotton samples were added to the dyebath (water+dyestuff) at room temperature and then temperature was raised to 60 °C with rate of 5 °C/min, 10 min after raising temperature to 60 °C sodium chloride (60 g/l) was added to the dyebath (in the cases of dyeing with salt) and after 30 min, sodium hydroxide (4 ml/l of 2M solution) was added for final fixation of reactive dyes on cotton. Dyeing continued at 60 °C for 60 min. After completion of dyeing, the dyed samples were rinsed thoroughly with hot water and soaped in soap solution for 5 min in 60 °C, then washed with tap water.

2.5.2.9 Measurement of wrinkle recovery angle, tensile strength, whiteness index and wash fatness

Wrinkle recovery angle (WRA) of the cotton samples was measured according to DIN 53891 with a Monsanto wrinkle recovery tester (Karl Frank GmbH, Weinheim-Birkenau). The tensile strength was determined according to DIN 53530 (Zwick Universal Test Device 1445). The whiteness index was evaluated according to CIE-Lab method using a ColorLight SPH850 spectrophotometer. WRA, tensile strength, and whiteness index were measured at least using 5 cotton samples and the mean value was recorded. Fastness of durable press effect against laundering was evaluated according to EN ISO 105-CO6: 1997 (liquor volume 150 ml, liquor-to-goods-ratio 1:30, ECE detergent 4 g/l, 30 min, 40 °C).

2.5.2.10 Evaluation of fastness properties of dyed fabrics

Washing fatness of dyed cotton fabrics was determined according to EN ISO 105-CO6: 1997 (liquor volume 150 ml, liquor ratio 1:30, ECE detergent 4 g/l, 30 min, 40 °C). The rubbing fastness of dyed cotton fabrics was measured, according to DIN EN ISO 105-X12 by a crock meter.

[1] o.w.f: on the weight of fabric

2.5.2.11 Color measurement of dyed fabrics

Color measurement was done by measuring the color strength K/S, where K is the light absorption coefficient and S is the scattering coefficient, according to the Kubelka Munk equation (Garland, 1993):

$$K/S = \frac{(1-R)^2}{2R}$$

Equation 3 Kubelka Munk equation

where R is the reflectance at the maximum wavelength. R was determined by the ColorLight SPH850 spectrophotometer.

2.5.2.12 Evaluation of flame retardancy of treated cotton by 45° flammability test

The flame retardancy of cotton fabrics were evaluated ASTM D1230-94 (45° flame test-"Standard Test Method for Flammability of Apparel Textiles.

2.5.2.13 Measurement of char yield

To measure the char yield, the weight of each conditioned cotton sample (24h, 20 °C, and 65% humidity) was weighed before and after burning. The char yield was calculated according to the following equation (Lessan et al. 2011):

$$\text{Char yield} = \frac{m2}{m1} \times 100$$

Equation 4 Char yield equation

where m_1 and m_2 are the weight of sample before and after burning, respectively.

2.5.2.14 Differential scanning calorimetry (DSC)

Also differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60/A, operating under nitrogen atmosphere and with initial sample weight of 10

mg. The DSC test process was done at temperature range of 50-500 °C and heating rate of 10 °C/min under a continuous flow of nitrogen.

2.5.2.15 Evaluation of biostatic properties of treated cotton

The biostatic properties of cotton samples were evaluated by Formazan test (Altman, 1976; Oppermann et al. 2003), which is based on the incubation of E.coli bacteria culture on the textile samples. E.coli culture medium (10 µl – 1 day old) was added to 20 ml distilled water in 50 ml Erlenmeyer flasks. The textile samples were cut to circular form (4 cm diameter) and put into the Erlenmeyer flasks. Then, the solutions were stirred at 37 °C for 4 hours (200 r/min).

After 4 hours, 1 ml of culture medium and 100 µl of triphenyltetrazoliumchloride (0.5 % w/v) were given to a sterile glass tube and shacked for 20 min for incubation. Afterward, 1 ml of sample was transferred to an Eppendorf-tupe and centrifuged for 3 min (4000 r/min). Then, 1 ml of ethanol was given and kept in ultrasound until the dye was dissolved. After a further centrifuge the absorption was measured at 480 nm in UV-Vis spectroscopy.

$$\text{Inhibition of bacteria growth (\%)} = \frac{Blank_{absorption} - Treated\ sample_{absorption}}{Blank_{absorption}} \times 100$$

Equation 5 Inhibition of bacteria growth

2.6 Results and discussion

2.6.1 Chemical characterization of carboxylated PVAm

The degree of substitution (DS) of carboxylated PVAm has been calculated from the C/N ratio. Due to the introduction of carboxylic groups in PVAm the C/N ratio changes. In Table 2.6.1 the results of elemental analysis are summarized. The C/N values have been obtained from the results of the elemental analysis and DS_{EA} are the calculated DS from these C/N values.

The chemical structure of the synthetized polyamino carboxylic acid was confirmed by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of PVAm showed two singlets at 2.2 and 4.1 ppm with peak area of 12.02 and 6.24, respectively. These peaks have been attributed to the protons in CH_2- and CH- $(-CH_2-CH-NH_2)_n$, respectively. The carboxylated PVAm showed a new triplet at 1.2 ppm, according to the protons of methylene group ($-CH_2$) adjacent to the carboxyl group. Therefore, a DS value can also be calculated from peak areas of ^{1}H-NMR spectra. The results are presented in Table 2.6.1.

Table 2.6.1 Experimental degree of substitution of carboxylated PVAm, calculated from C/N ratio of elemental analysis (DS_{EA}) and peak area ($PA_{1H\text{-}NMR}$) of ^{1}H-NMR ($DS_{1H\text{-}NMR}$)

Mole ratio PVAm : bromoacetic acid [±0.01]	**C/N**	**DS_{EA} [%]**	**$PA_{1H\text{-}NMR}$**	**$DS_{1H\text{-}NMR}$ [%]**
1.00 : 0.00	1.7	0	0	0
1.00 : 0.25	2.1	22.5	0.87	21.7
1.00 : 0.50	2.5	48.7	1.69	42.2
1.00 : 0.75	2.9	69.6	2.47	61.7
1.00 : 1.00	3.3	94.6	3.89	97.5

Infrared spectroscopy (FTIR) was as well used to obtain information about the chemical structure of carboxylated PVAm. In Figure 2.6.1 the FTIR spectra of PVAm and carboxylated PVAm are given. The spectrum of PVAm showed a signal at 1670 cm^{-1} and a broad signal at 3369 cm^{-1}, attributed to the primary amine group ($-NH_2$) and NH_2- stretching, respectively. The signal at 1175 cm^{-1} has been attributed to the stretching of C-N bond. As it can be seen from the spectrum of the carboxylated PVAm (DS 22.5%), a new intense peak was seen at 1735 cm^{-1}, belonging to the carboxyl group (-COOH). The appearance of this signal confirmed the carboxylation of PVAm, too. With increasing degree of substitution the intensity of carboxyl bond at 1735 cm^{-1} also increased.

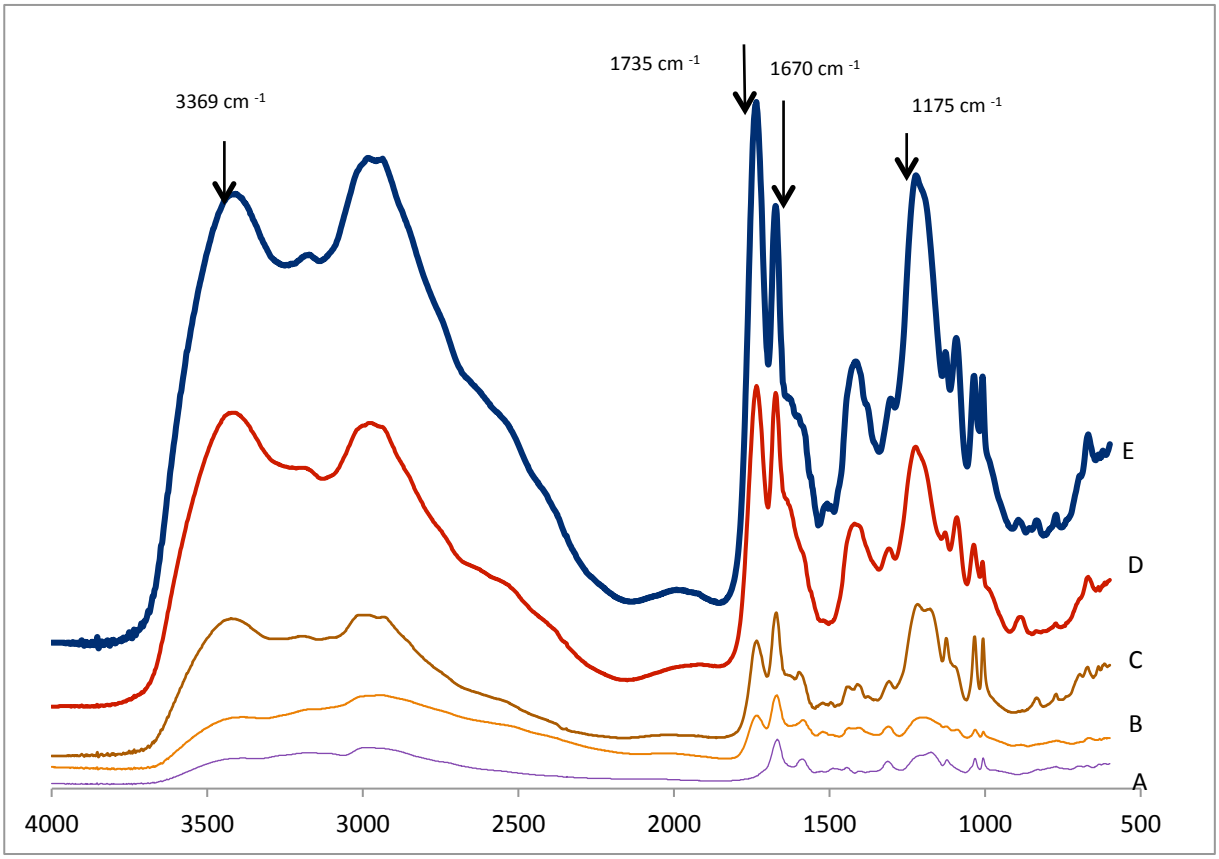

Figure 2.6.1 FTIR-spectra of PVAm (A) and carboxylated PVAm of different degree of substitution (DS)

B: DS 22.5%, C: DS 48.7%, D: DS 69.6% and E: DS 94.6%

2.6.2 Gravimetric test of treated cotton with carboxylated PVAm

In Figure 2.6.2 the relationship between the amounts of fixed carboxylated PVAm on cotton as a function of concentration of the carboxylated PVAm in solution (DS 94.6%) is shown. With increasing concentration of carboxylated PVAm the weight of the finished cotton increased, indicating the successful fixation of the carboxylated PVAm. The solution with an initial concentration of carboxylated PVAm of 8% in dipping process has resulted to a weight increase of 3.4%.

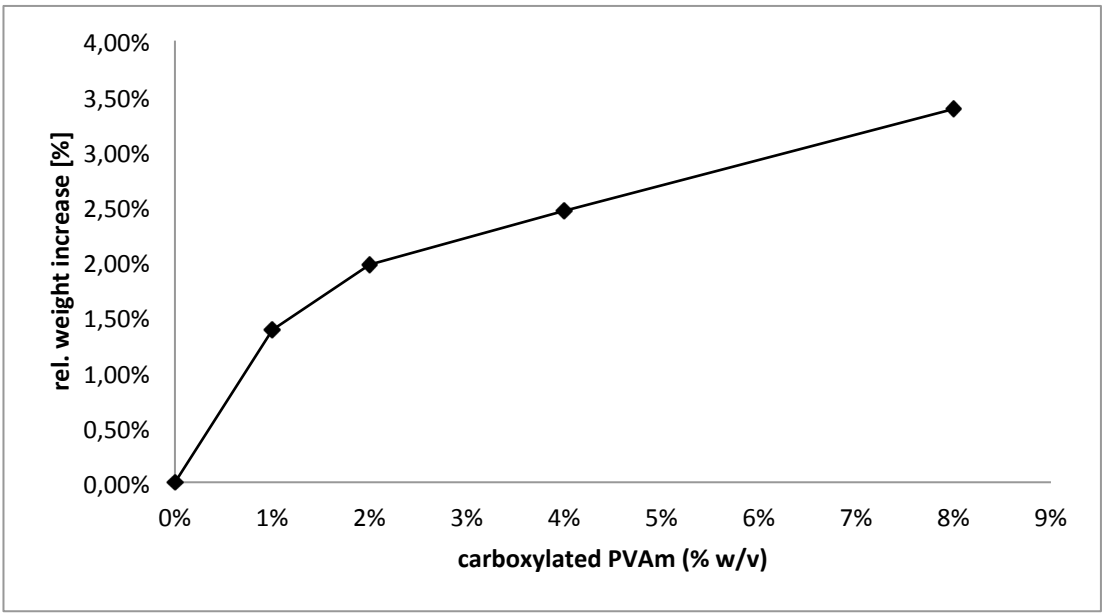

Figure 2.6.2 Relative weight increase of finished cotton with carboxylated PVAm vs. concentration of carboxylated PVAm (DS 94.6%)

In Figure 2.6.3 the weight of the finished cotton samples as a function of the degree of substitution of the carboxylated PVAm used is given. Figure 2.6.3 shows that with increasing the degree of substitution (DS) relative weight of finished fabric increased and approving the permanent fixation of the polyamino carboxylic acid on the cotton fabric.

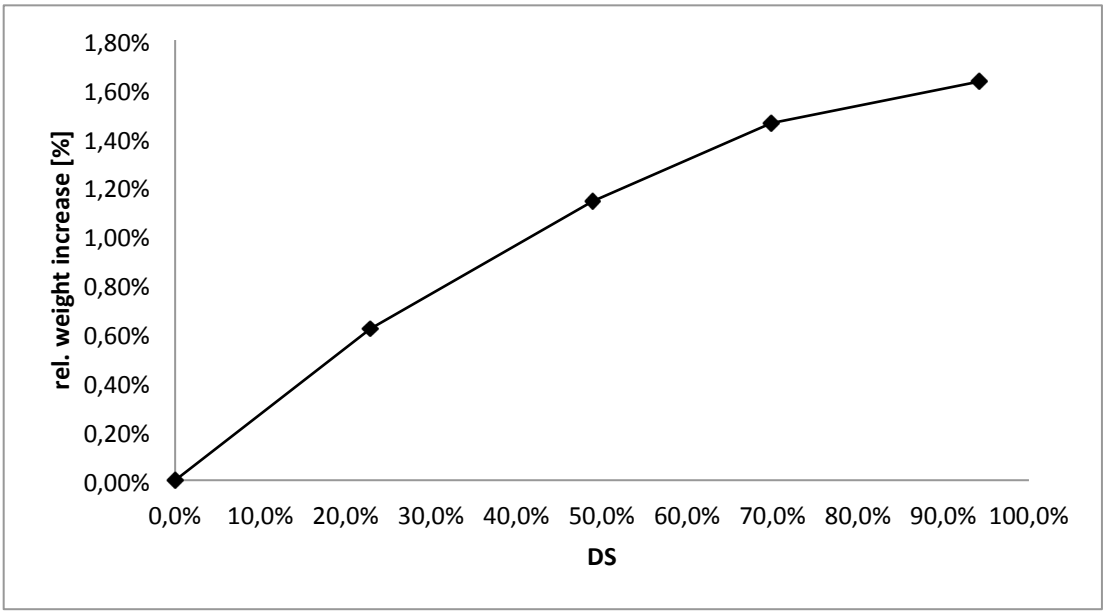

Figure 2.6.3 Relative weight increase of finished cotton with carb. PVAm (1% w/v) vs. degree of substitution (DS)

2.6.3 FTIR-spectroscopy of the finished cotton

Fixation of the synthetized polyamino carboxylic acid on the cotton fabric has occurred through the formation of ester bond. The FTIR spectrum of cotton finished with polyamino carboxylic acid (DS 94.6%) showed a signal at 1730 cm^{-1}. This signal has been attributed to the ester bond and confirmed the esterification of the finished cotton (Yang C., 1991a; Gillingham, Lewis, & Voncina, 1999). The FTIR spectrum of the finished cotton is presented in Figure 2.6.4. It has been suggested by some authors that esterification of cotton can occur through formation of 5-member or 6-member cyclic anhydride intermediates, which easily reacts with the hydroxyl groups of the cellulose chain (Yang & Wang, 1996; Yang & Wang, 1997; Welch, 1994; Gillingham, Lewis, & Voncina , 1999; Yang C. , 1993c). However, esterification via formation of n-member cyclic anhydrides has been reported, too (Martel et al. 2002, Martel et al. 2000). This may be a possible mechanism for the reaction of the carboxylated PVAm with cotton.

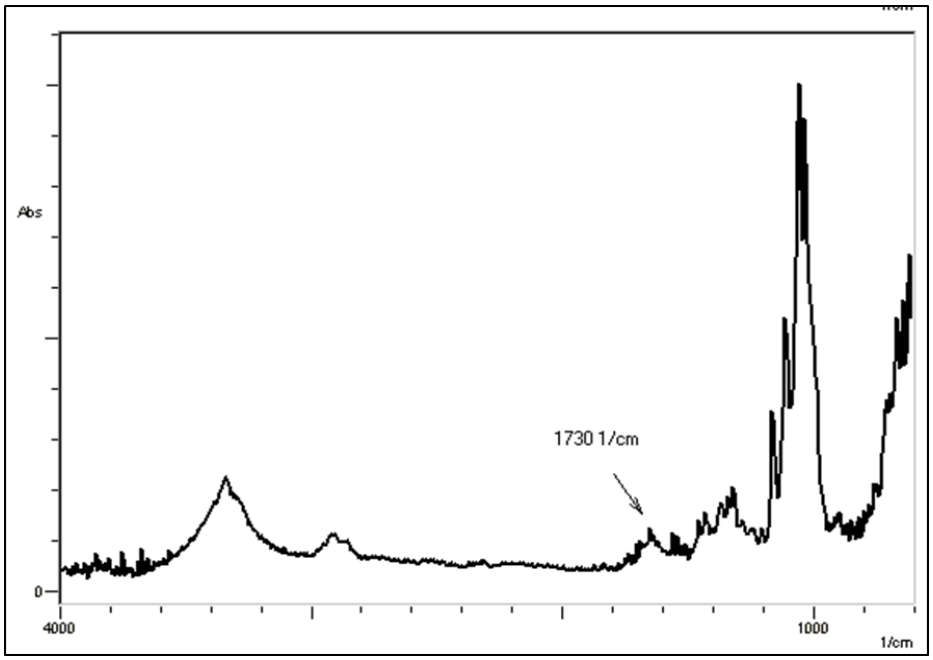

Figure 2.6.4 FTIR-spectrum of cotton finished with carboxylated PVAm (DS 94.6%, 1% w/v)

2.6.4 Determination of carboxyl group content

Regarding to the crosslinking mechanism it can be supposed that the additional free carboxylic groups in the carboxylated PVAm which are accessible in cellulose reflects the effectiveness of cotton crosslinking. Thus, the quantitative measurement of free carboxylic groups in cotton is useful to evaluate the effectiveness of crosslinking (Sauperl & Ribitsch, 2009). The amount of free carboxylic groups present on the finished cotton as a function of the degree of substitution of carboxylated PVAm is shown in Figure 2.6.5. As expected, with increasing the number of carboxylic groups bound to the PVAm, the amount of unreacted carboxylic groups on the cotton fabric increased.

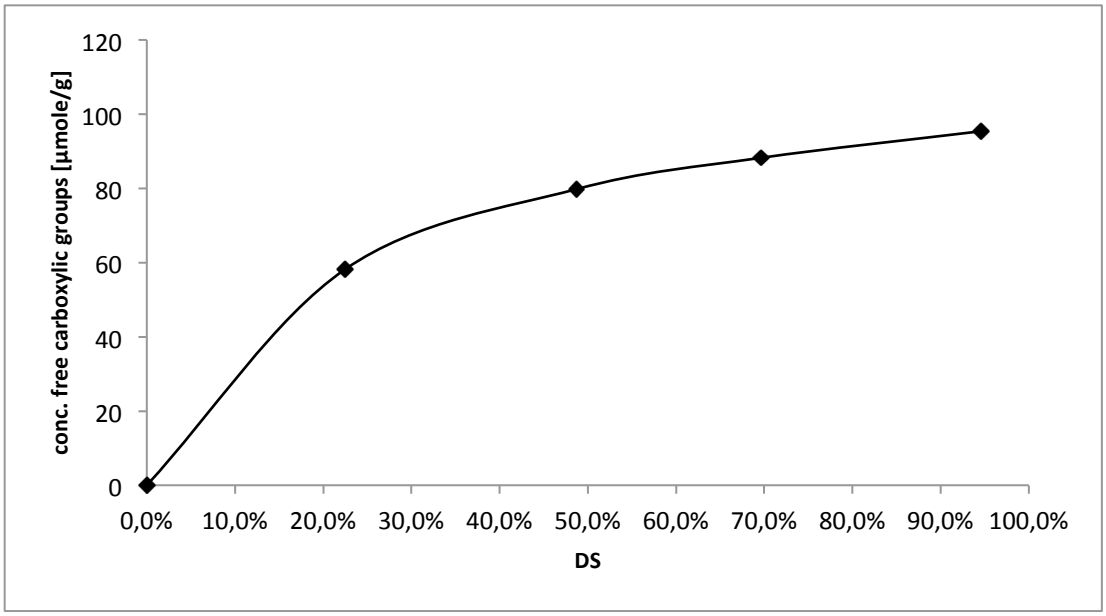

Figure 2.6.5 Concentration of free carboxyl groups in finished cotton with carboxylated PVAm (1% w/v) vs. degree of substitution (DS)

2.6.5 Measurement of free amino groups in treated cotton with carboxylated PVAm

After fixation of carboxylated PVAm the number of accessible amino groups was determined with the help of potentiometric titrations. The results are summarized in Figure 2.6.6. As expected, with increasing values of DS the number of free amino groups decreases.

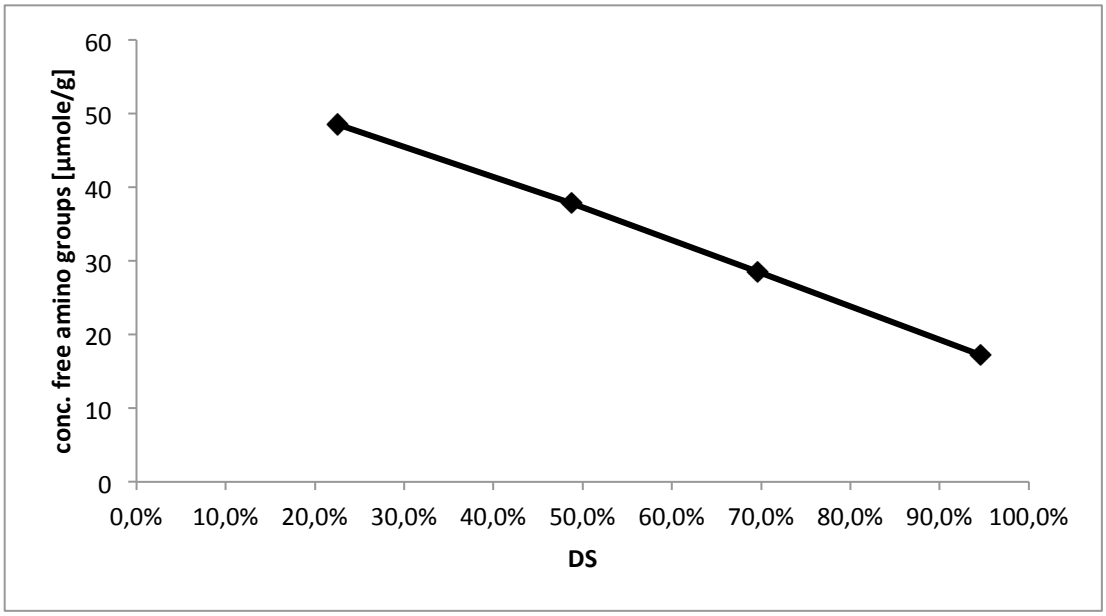

Figure 2.6.6 Concentration of free amino groups in finished cotton with solution of carboxylated PVAm (1% w/v) vs. degree of substitution (DS)

2.6.6 Evaluation of durable-press properties of the cotton finished with carboxylated PVAm

2.6.6.1 Durable-press effect of carboxylated PVAm with bromoacetic acid

Wrinkle recovery angle (WRA) of cotton fabrics with 1% (w/v) solution of carboxylated PVAm with different degrees of carboxylation was measured to evaluate the performance of durable-press induced by carboxylated PVAm. The results are presented in Table 2.6.2. Also the durability of the obtained easy-care properties to laundry washing was also evaluated.

Table 2.6.2 Wrinkle recovery angle (WRA°) of the original cotton (0) and the cotton finished with carboxylated PVAm (1% w/v) of different degrees of substitution (DS), and its durability against laundry washing

(No. washing cycles: 1-5)

DS [%]	WRA°	$WRA°_1$	$WRA°_5$	Loss in WRA°-after 5 washing cycles [%]
0	101	-	-	-
22.5	114	104	102	11.7
48.9	123	116	111	10.8
69.8	137	129	125	9.6
94.2	161	152	148	8.7

These results show that the use of carboxylated PVAm produced a durable press effect in the finished fabric. The improvement of this effect depends on the number of ester bonds formed between the hydroxyl groups of cellulose and the carboxyl groups in the polycarboxylic acids (Trask-Morrell, Kottes Andrews, & Graves, 1990; Welch, 1988; Welch, 1990). The wrinkle recovery angle from 101° in original cotton improves to 161° in the cotton finished with carboxylated PVAm (DS 94.6%).

Also in Table 2.6.2 the durability of this easy-care effect after 5 washing cycles is given. The durable-press effect was only reduced by 9% in the case of cotton finished with carboxylated PVAm with a DS value of 94.2%. With increasing number of ester bonds, the number of unhydrolyzed ester bonds and consequently the wash resistance of the durable press effect increased.

When the curing process is carried out in a proper temperature (140-190°C) during a sufficient time (90s – 7min), the formed ester linkage is resistant to multiple alkaline laundering (Schramm et al. 1998; Yang, 1991a; Welch, 1988; Welch & Andrews, 1989a).

In Table 2.6.3 the results of tensile strength and whiteness index of cotton fabrics treated with 1% w/v solution of carboxylated PVAm and different degrees of substitution.

Table 2.6.3 Tensile strength and whiteness index of the original cotton (0) and the cotton finished with carboxylated PVAm (1% w/v) of different degrees of substitution (DS)

DS [%]	Tensile Strength		Whiteness Index	
	Measured tensile strength [N]	Loss of tensile strength [%]	Measured whiteness index	Loss of whiteness [%]
0	527	-	78	-
22.5	511	3.13	43	81.4
48.9	501	5.19	54	44.4
69.8	455	15.82	58	34.5
94.2	416	26.69	64	21.2

Table 2.6.3 shows that creation of durable-press effect by crosslinking of cellulose chains with ester bonding will lead to a reduction of tensile strength of treated cotton, because crosslinking of cellulose inhibits distribution of tear stress over many molecules which can slightly shift the external forces (Schindler & Hauser, 2004). Also, the acidity of the finishing solution is another cause of reducing the tensile strength. However, decrease of tensile strength in treated cotton with carboxylated PVAm is not as much as treated cotton textiles with conventional polycarboxylic acids. Generally durable-press finishing of cotton fabric with polycarboxylic acids or formaldehyde-based chemicals will lead to yellowing of treated cotton. Durable-press finishing of cotton by the carboxylated PVAm caused also yellowing of cotton, but an inverse trend is seen for changes in whiteness of treated cotton: by increase the formation of ester bonds, whiteness index is improved. On the other hand, the observed yellowing in comparison to treated cotton with conventional crosslinking agents is normal.

2.6.6.2 Carboxylation with 3-bromopropionic acid

The carboxylation of polyamines with other halocarboxylic acids is also possible. Polyvinylamine can also be carboxylated with 3-bromopropionic acid. Figure 2.6.7 shows the reaction of 3-bromopropionic acid with a given polyamine.

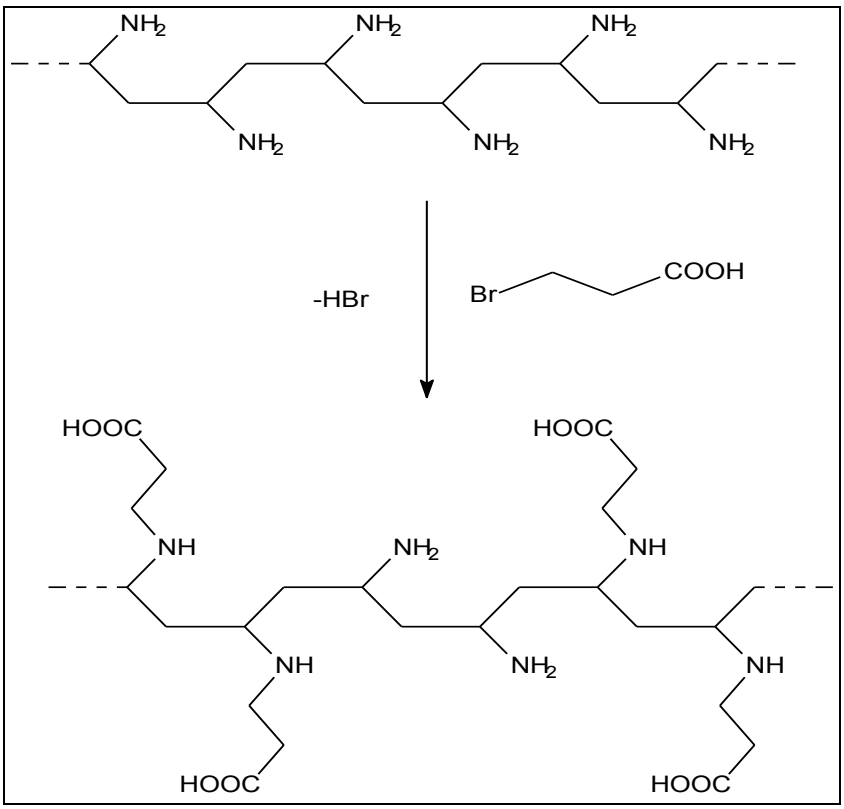

Figure 2.6.7 Reaction of 3-bromopropionic acid with a polyamine

The 1% w/v solutions of PVAm were carboxylated with 3-bromopropionic acid and the degree of substitution was determined by elemental analysis. The results of elemental analysis are presented in Table 2.6.4.

Table 2.6.4 Experimental degree of substitution of carboxylated PVAm with 3-bromo-propionic acid, calculated from C/N ratio of elemental analysis (DSEA)

C/N	DS_{EA} [%]
1.7	0
2.3	23.1
2.9	47.3
3.5	68.8
4.2	95.4

The carboxylated PVAm with 3-bromopropionoc acid (PACA-BP) was applied on the cotton fabric by pad-dry-cure method. Then the durable-press finishing effect and its durability against laundry washing were evaluated. The results are summarized in Table 2.6.5.

Table 2.6.5 Wrinkle recovery angle (WRA°) of the original cotton (0) and the cotton finished with carboxylated PVAm (1% w/v) of different degrees of substitution (DS) and its durability against laundry washing

(No. washing cycles: 1-5)

DS [%]	WRA°	$WRA°_1$	$WRA°_5$
0	101	-	-
23.1	117	110	107
47.3	124	119	112
68.8	136	124	115
95.4	149	140	136

Table 2.6.5 shows that, PACA-BP had also the same durable-press finishing effect, like carboxylated PVAm with bromoacetic acid (PACA-B). Also the resulted effect had a good washing fastness. Figure 2.6.8 compares the durable-press effect

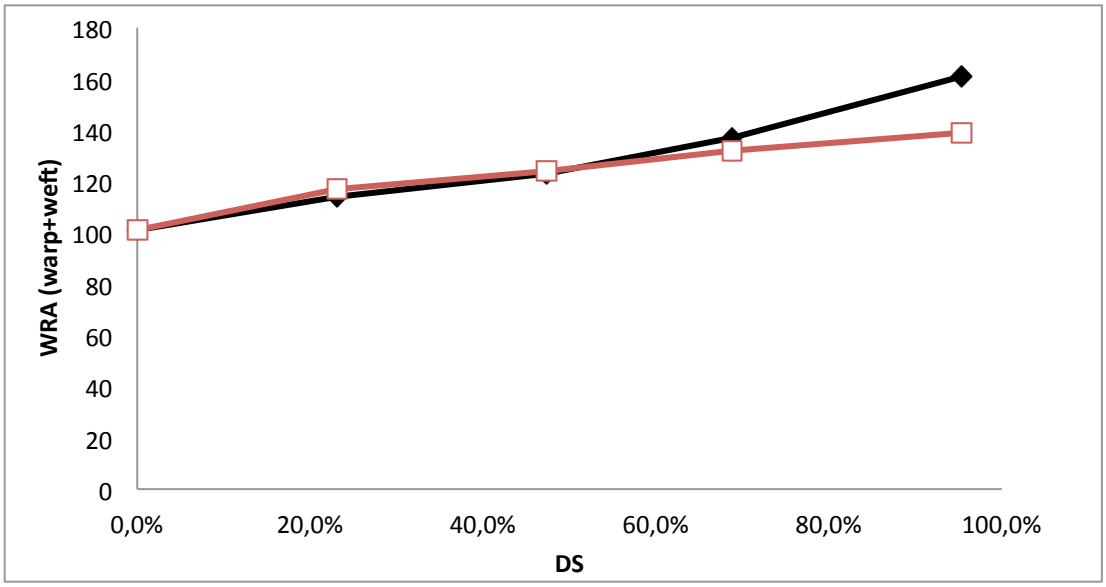

Figure 2.6.8 Comparison of PACA-B (•) and PACA-BP (□) in the case of durable-press effect (wrinkle recovery angle-WRA)

between carboxylation with bromoacetic acid and 3-bromopropionic acid. As it can be seen, there is not any great difference in their effect.

In Table 2.6.6 the results of tensile strength and whiteness index of cotton finished with 1% w/v solution of PACA-B and PACA-BP. It shows that, PACA-BP in comparison with PACA-B has less negative impact on the tensile strength and whiteness index of treated cotton.

Table 2.6.6 The results of tensile strength (T.S) and whiteness index (W.I) of original cotton (0) and cotton finished with 1% w/v solutions of PACA-B and PACA-BP

DS [%]		**T.S [N]**		**Loss of T.S [%]**		**W.I**		**Loss of W.I [%]**	
PACA-B	PACA-BP	PACA-B	PACA-BP	PACA-B	PACA-BP	PACA-B	PACA-BP	PACA-B	PACA-BP
0	0	527	527	-	-	78	78	-	-
22.5	23.1	511	517	3.0	1.9	43	50	44.9	35.9
48.9	47.3	501	505	4.9	4.2	54	59	30.8	24.4
69.8	68.8	455	488	13.7	7.4	58	64	25.6	17.9
94.2	95.4	416	451	21.1	14.4	64	69	17.9	11.5

With regard to the obtained results, it seems that generally there is not any outstanding difference between PACA-B and PACA-BP in the final effect of durable press finishing. Although, whiteness and tensile strength of the cotton finished with PACA-BP was better than PACA-B.

2.6.6.3 Determination of the optimal process parameters

The most important process parameters are catalyst, pH and curing temperature, which play a crucial role in final effect of polycarboxylic acids as durable-press finishing agents (Yang, 1993d; Yang, 1993a).

Sodium hypophosphite is the best catalyst for crosslinking of cotton with polycarboxylic acids. Because the highest levels of durable press rating and wrinkle recovery angle, reduction in cure temperature, increase of tensile strength retention and most satisfactory whiteness are obtained with polycarboxylic acids in the presence of this catalyst (Welch, 1990; Rowland et al. 1967; Gu & Yangm, 2000; Lammermann, 1992; Welch & Peter, 1997). The mechanism of esterification of cotton with polycarboxylic acids in presence of sodium hypophosphite is presented in Figure 2.6.9 (Gu & Yang, 2000; Gillingham et al. 1999). Sodium hypophosphite

reacts with cyclic anhydride intermediate of polycarboxylic acids and finally reacts with cellulose.

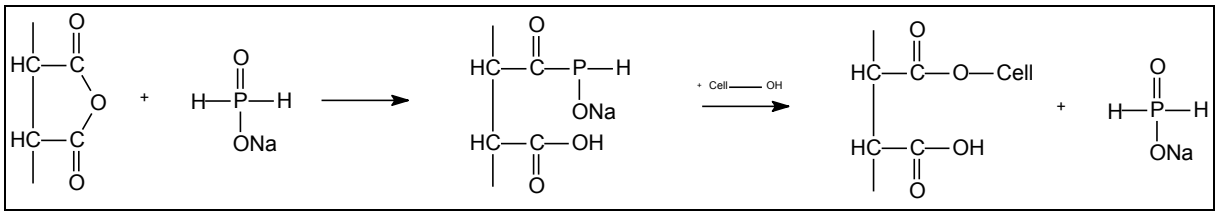

Figure 2.6.9 Cotton esterification with polycarboxylic acids in presence of sodium hypophosphite

Also in this study, sodium hypophosphite was used as catalyst. The effect of sodium hypophosphite on durable-press properties of cotton treated with 1% w/v solution carboxylated PVAm with DS 94.2% and different concentration of sodium hypophosphite is presented in Figure 2.6.10.

Improvement of wrinkle recovery angle with increasing amount of catalyst used up

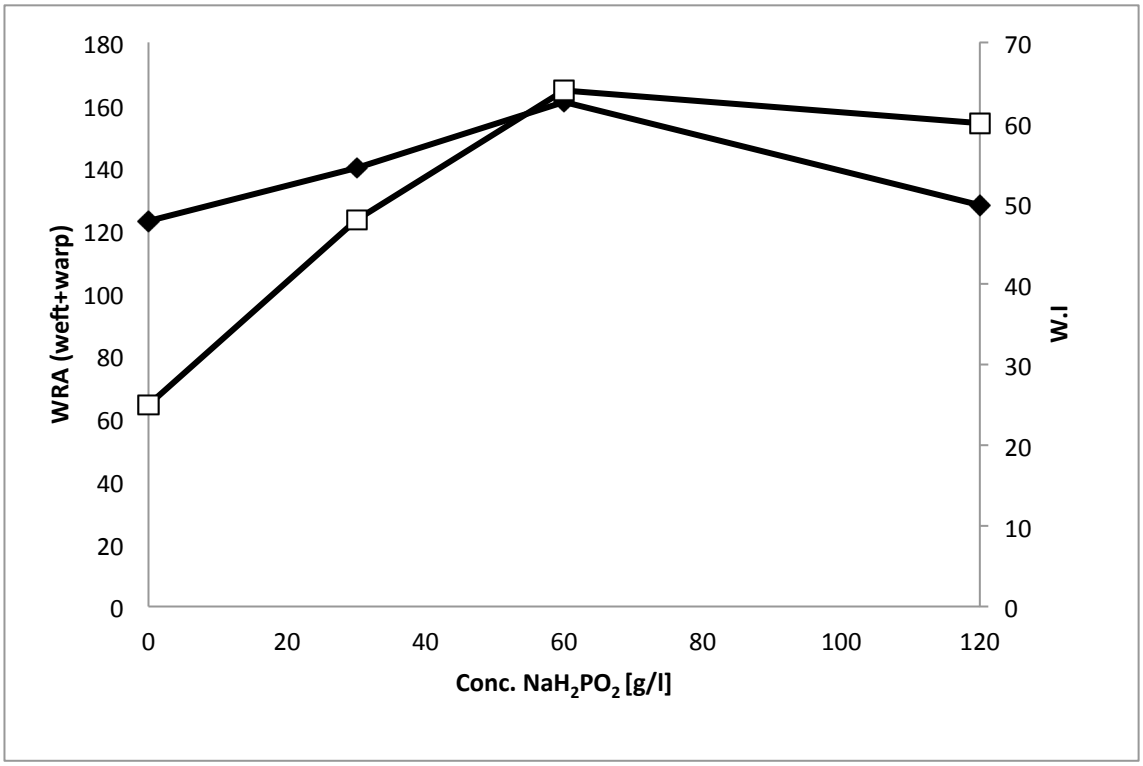

Figure 2.6.10 The effect of concentration of sodium hypophosphite on wrinkle recovery angle (WRA-•) and whiteness index (W.I-□) of cotton treated with 1% w/v solution carboxylated PVAm (DS 94.6%)

to 60 g/l indicates the positive effect of catalyst in formation of ester bonds. However, using higher concentrations of sodium hypophosphite (120 g/l) caused no more improvement in performance of polycarboxylic acid. Thus, the optimum amount of catalyst in these experiments was 60 g/l. On the other hand, the presence of sodium hypophosphite led to an improvement of the whiteness index of treated cotton.

The esterification by polycarboxylic acid is also pH-dependent. Yang showed that when a cotton fabric is finished with BTCA without a catalyst, the number of formed ester linkage in the fabric and the effectiveness of bonded BTCA molecules decreases as the pH of finishing bath increased from 1.5 to 5.5. This occurs, when also a catalyst is used. It has been attributed to the fact that the quantity of cyclic anhydride intermediate formed in the cotton fabric increased as the pH in finishing bath decreases. Therefore, formation of cyclic anhydride intermediate is accelerated by increased proton concentration of finishing bath. So it is important to determine the optimum pH range of finishing bath to achieve the best results (Yang, 1993a; Yang, 1993b).

In order to evaluate the effect of pH on final effect of polyamino carboxylic acids as durable-press finishing agents, a 1% w/v solution of carboxylated PVAm (DS 94.2%) was applied onto cotton fabric in presence of 60 g/l sodium hypophosphite by pad-dry-cure process (170 °C – 6 min) with variable pH values. Figure 2.6.11 shows the effect of pH on WRA and whiteness index of the finished cotton.

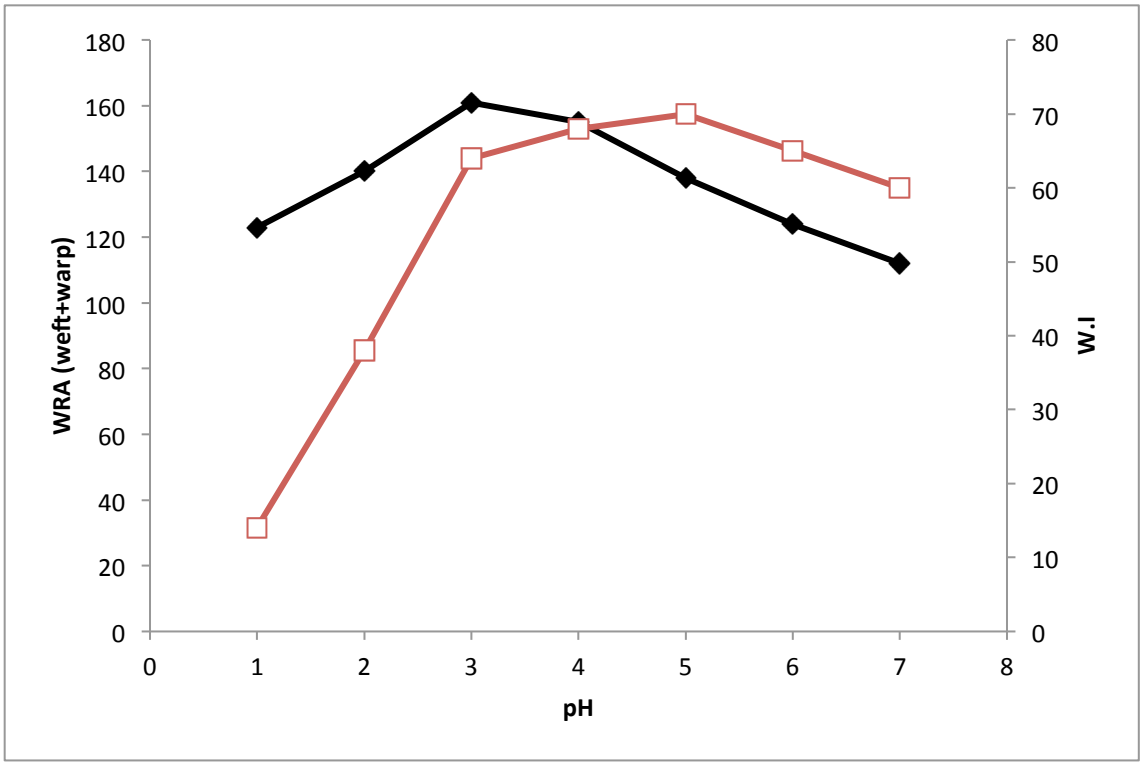

Figure 2.6.11 The effect of pH on wrinkle recovery angle (WRA-•) and whiteness index (W.I-□) of cotton finished with 1% w/v solution carboxylated PVAm (DS 94.2%)

With increasing pH value from 1 to 3 the wrinkle recovery angle (WRA) of the finished cotton improved (from 123 ° a pH 1 to 161 ° at pH 3) and then by further increase in pH from 3 to 7 (from acidic condition to neutral point), WRA decreased. It means that the optimum pH is 3. On the other hand, in lower pH values, fabric tends to become yellower. In pH values less than 3, the finished cotton was extreme yellow, specifically in pH 3. At pH 5, loss of whiteness was at least (whiteness index 70), but the most successful WRA was seen at pH 3. With regards to insignificant difference of whiteness of the finished cotton at pH 3 and pH 5 (63 and 70, respectively) and the obtained WRA in these pH values, it seems that the suitable pH could be 3. Investigating the changes of tensile strength of treated cotton at different pH values certified this result.

The effect of pH on tensile strength of the finished cotton is given in Figure 2.6.12.

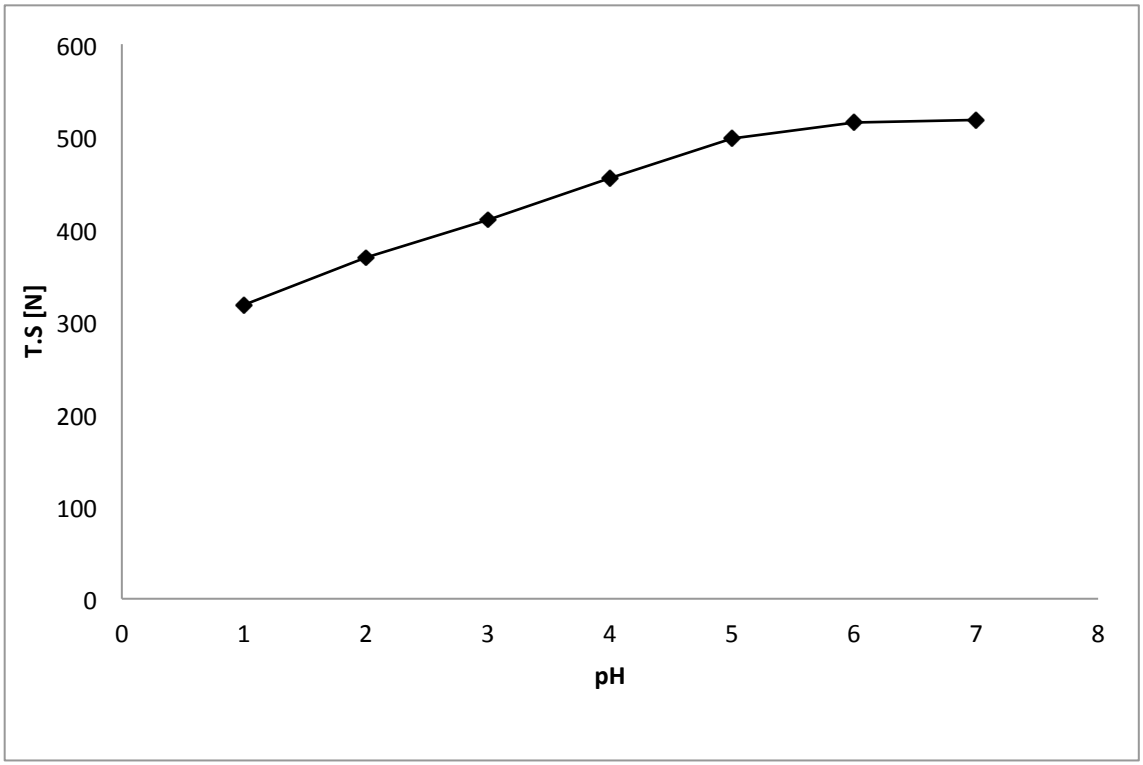

Figure 2.6.12 The effect of pH on the tensile strength (T.S) of the cotton finished with carboxylated PVAm (DS 94.2%)

Increase of pH improved the tensile strength of the finished cotton. The tensile strength increased sharply by increase of pH from 1 to 5 and from this point came the increasing rate had a slow slope. Consequently, by concerning the obtained results: wrinkle recovery angle, whiteness index and tensile strength, the suitable pH for finishing of cotton fabric with carboxylated PVAm, pH values between 3 and 4 can be safe and optimum.

2.6.7 Evaluation of flame retardancy properties of the finished cotton with carboxylated PVAm

The 45° flammability test (ASTM D1230-94) was used to measure and describe the properties of fabrics in response to heat and flame, which was based on measurement of two factors: ease of ignition and flame spread time (Yang & Qiu, 2006). Then the tested samples were categorized into three classes:

Class I: These textiles were considered to be generally acceptable for apparel, defined according to the following conditions:

a) Textiles without raised fiber surface but with an average time of flame spread of 3.5 seconds or more.

b) Textiles with a raise fiber surface and average time of flame spread of more than 7 seconds or burning with a surface flash (in less than 7 seconds), in which the base fabric is not affected by flame (no base burn).

c) Textiles with no ignition.

Class II: These textiles were considered are categorized as intermediate between class I and class III, defined according to the following conditions:

a) Textiles with raised fiber surface and average time of flame spread between 4 and 7 seconds, in which the base is ignited, charred or melted.

Class III: These textiles were considered as unsuitable for apparel, defined according to the following conditions:

a) Textiles without raised fiber surface and average time of flame spread time of less than 3.5 seconds.

b) Textiles with a raised fiber surface and average time of flame spread of less than 4 seconds, in which the base is ignited, charred or melted.

In Table 2.6.7 the results of 45° test of cotton finished with 4% v/w solution of carboxylated PVAm of different degrees of substitution (DS) and in the presence of sodium hypophosphite (30 g/l) as phosphorus-catalyst.

Table 2.6.7 The results of 45°-flam test of original cotton (0) and cotton finished with carboxylated PVAm of different degree of substitution (DS) and sodium hypophosphite (30 g/l)

DS [%]	average burning time (s)	No. samples with SB	No. samples with BB	classification
0	1.2	5	5	3
22.9	1.2	5	4	3
48.9	1.2	5	2	2
69.8	1.2	5	0	1
94.2	1.2	5	0	1

The results show that finishing of cotton fabric with carboxylated PVAm in presence of NaH_2PO_2 reduces the flammability of cotton fabric. The effectiveness of finishing is depending on the value of DS. With increasing degree of substitution of the carboxylated PVAm the flammability of the finished cotton reduces due to the formation of more ester bonds. According to the results of 45°-flam test of the cotton finished with carboxylated PVAm and a DS value of 22.9%, four samples showed base burn (BB) and it failed the flammability test with the ranking of class 3. In the case of the cotton finished with carboxylated PVAm and DS value of 94.6% none of the samples had BB and it was categorized in class I.

Table 2.6.8 shows the results of 45°-flam test of the finished cotton after 5 cycles of laundry washing. The results indicate that, the flame retardancy of the finished cotton fabrics is durable to the multiple laundering and increases as the DS value of the carboxylated PVAm used increases. Flame retardancy of the cotton finished with the DS values of 69.8% and 94.2% showed the highest durability to laundry washing.

Table 2.6.8 The results of 45°-flam test of original cotton (0) and cotton finished with carboxylated PVAm of different degree of substitution (DS) and sodium hypophosphite (30 g/l), after five cycles of laundering washing

DS [%]	average burning time (s)	No. samples with SB	No. samples with BB	classification
0	1.2	5	5	3
22.9	1.2	5	5	3
48.9	1.2	5	3	3
69.8	1.2	5	1	1
94.2	1.2	5	0	1

Sodium hypophosphite (NaH_2PO_2) as phosphorus-containing catalyst plays an important role in flame retarding of cotton with polycarboxylic acids. It helps to esterify cotton fabric through formation of cyclic anhydride intermediates at higher temperatures (Wu & Yang, 2009; Cheng & Yang, 2009a; Cheng & Yang, 2009b; Wu, Yang, & He, 2010). Moreover, NaH_2PO_2 helps to form more chars (Wu & Yang, 2008; Gaan & Sun, 2009; Yang & Qiu, 2007; Zhu et al. 2004; Gaan & Sun, 2007a; Gaan & Sun, 2007b). In Table 2.6.9 the results of 45°-flam test of cotton finished with carboxylated PVAm (DS 94.6%) at different concentrations of NaH_2PO_2 are given. They show that the flammability of the finished in absence of sodium hypophosphite was not reduced and four samples showed burn base. The flammability of the finished cotton fabrics decreased with increasing concentrations of NaH_2PO_2. Thus, the cotton samples finished at higher concentrations of sodium hypophosphite (45 and 60 g/l) passed the 45°-flam test and were categorized to the class I.

Table 2.6.9 The results of 45° flammability test of cotton samples treated with 4% w/v solutions of carboxylated PVAm (DS 94.6%), in presence and absence of sodium hypophosphite

Conc. NaH_2PO_2 [g/l]	**average burning time (s)**	**No. samples with SB**	**No. samples with BB**	**classification**
0	1.2	5	4	3
15	1.2	5	2	2
30	1.2	5	2	2
45	1.2	5	0	1
60	1.2	5	0	1

In Table 2.6.10 the char yield of original cotton and the cotton fabrics finished with carboxylated PVAm, under different conditions of application are summarized. The results of durability of the flame retardancy effect to laundry washing are included.

The char yield of original cotton fabric was 0.38 g after five cycles of washing and the finishing of cotton with carboxylated PVAm has effectively increased the char yield. However, the char yield was somehow reduced after five washing cycles. The flame retardancy of the finished cotton for a given concentration of carboxylated PVAm depends on the DS value. With increasing concentration of NaH_2PO_2 the char yield increases. The best flame retardancy was obtained when the cotton fabric was finished with carboxylated PVAm (DS 94.6%) and 60 g/l NaH_2PO_2. The char yield of this finished cotton after one washing was 25.2% and after five cycles of washing was 32.5%.

Table 2.6.10 Char yield of original cotton (0) and cotton finished with carboxylated PVAm of different degree of substitution (DS) and sodium hypophosphite (different concentrations)

DS [%]	Conc. NaH_2PO_2 [g/l]	Char Yield [%]	
		After 1 cycle of laundering	After 5 cycles of laundering
0	-	0.5	0.4
22.9	0	5.4	2.1
22.9	15	8.2	5.3
22.9	30	10.5	6.4
22.9	45	11.4	8.7
22.9	60	13.5	10.9
48.9	0	7.3	5.9
48.9	15	9.3	7.1
48.9	30	12.6	10.7
48.9	45	14.3	11.1
48.9	60	16.2	12.6
69.8	0	10.3	7.4
69.8	15	13.7	10.1
69.8	30	17.9	12.4
69.8	45	19.6	13.4
69.8	60	21.5	15.2
94.2	0	14.6	11.4
94.2	15	18.5	14.7
94.2	30	20.1	16.1
94.2	45	23.9	20.5
94.2	60	25.2	23.8

Differential scanning calorimetry (DSC) was used to investigate the pyrolysis properties of the finished cotton. Pyrolysis is a complex process with several reactions; including endothermic bond rupture, volatilization and finally formation of exothermic bond (Perkins et al. 1966). Figure 2.6.13 shows the DSC graphs of the original cotton and the cotton fabrics finished with PACA (different values of DS) and NaH_2PO_2 (60 g/l).

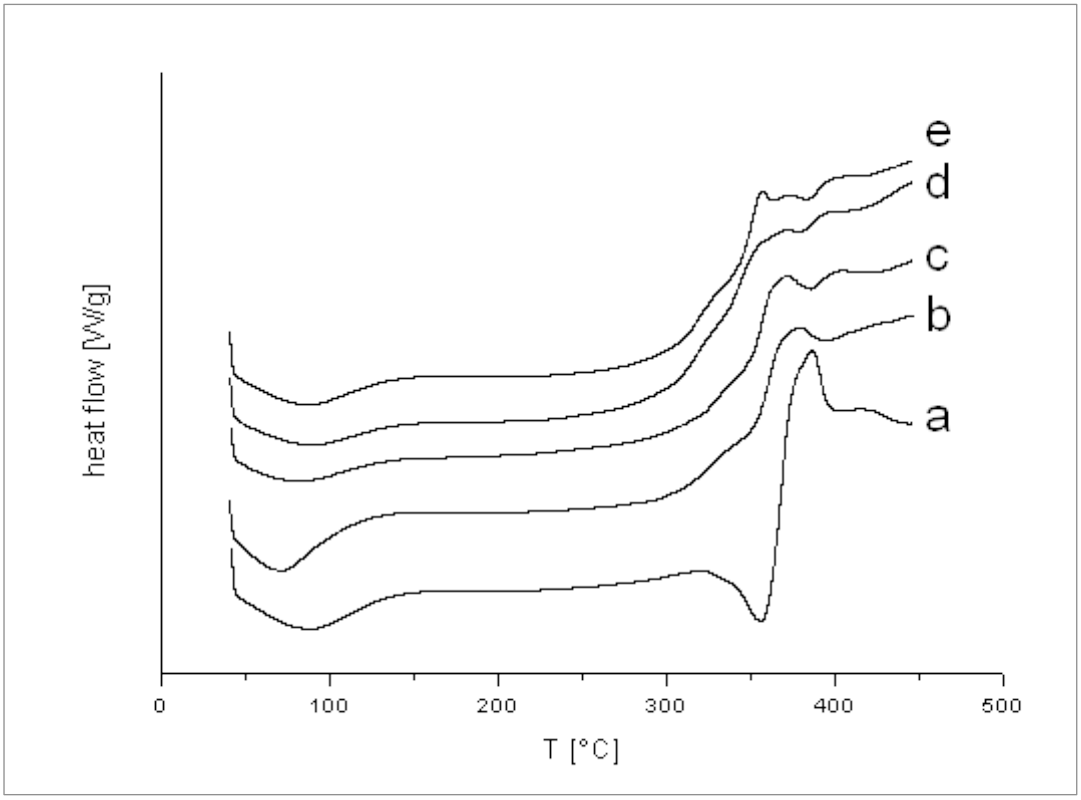

Figure 2.6.13 DSC curves of original cotton (a), cotton finished with PACA and DS 22.5% (b), DS 48.7% (c), DS , 69.6% (d) DS 94.6% (e), in presence of 60 g/l sodium hypophosphite

In curve of the original cotton a large endothermic peak in main pyrolysis stage is observed, which can be attributed to the vaporization of pyrolysis products (Dastjerdi et al. 2010). Cotton fabrics finished with PACAs and NaH_2PO_2 showed an exothermic peak in DSC graph. This peak was even observed when the PACA with lowest value of DS was used (Figure 2.6.13, graph b).

Also the DSC can be used to investigate the effect of NaH_2PO_2 on the flammability of cotton fabric. DSC graphs of finished cotton with 4% w/v solutions of carboxylated PVAm (DS 94.6%) in presence of different concentrations of sodium hypophosphite are given in Figure 2.6.14. It can be observed that with increasing the concentration of sodium hypophosphite the heat flow of the finished cotton increases.

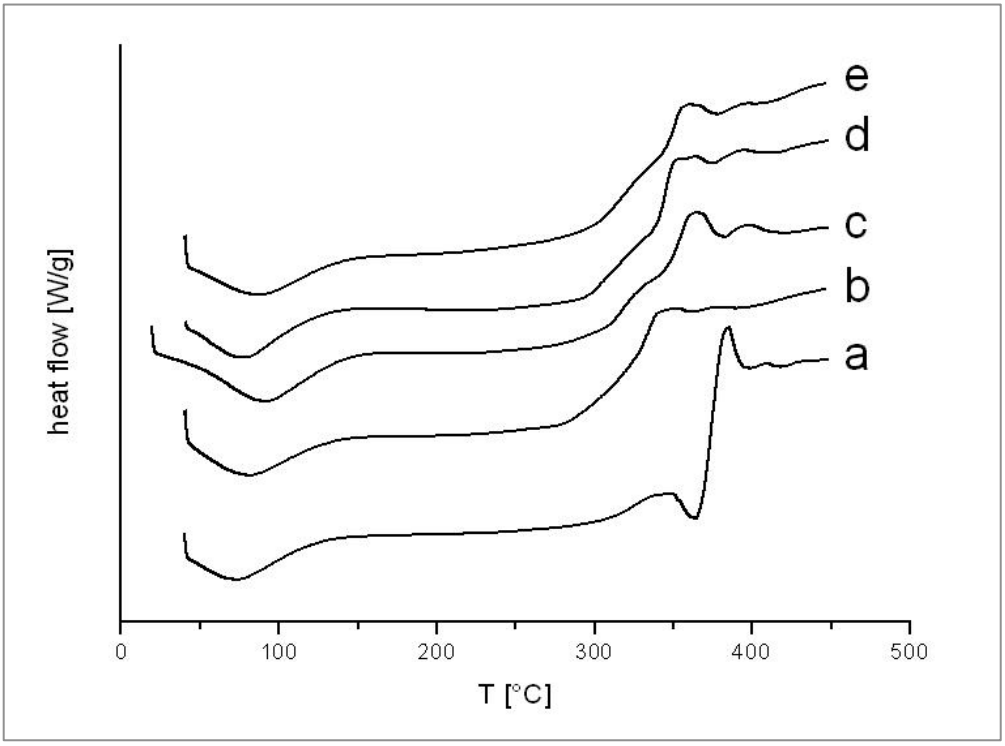

Figure 2.6.14 DSC curves of the original cotton (a) and the cotton finished with carb. PVAm (DS 94.6%) in presence of sodium hypophosphite 15 g/l (b), 30 g/l (c), 45 g/l (d) and 60 g/l (e)

2.6.8 Further effects of treated cotton with carboxylated PVAm

2.6.8.1 Biostatic properties of finished cotton with carboxylated PVAm

Generally there are several methods to classify the mechanism of antimicrobial activity. Based on these methods, the antibacterial products can be divided into biocides and biostats, leaching and bound antimicrobials, controlled-release and barrier-forming agents, and finally with regarding to their durability to the washing and laundering agents of poor and of good washing resistance (Simoncic & Tomsic, 2010; Schindler & Hauser, 2004; Dring, 2003). The activity of antimicrobial compounds for textile finishing can be biostatic or biocidal. Biocides (including bactericides and fungicides) can kill bacteria and fungi, while the biostats (bacteriostats and fungistats) inhibit the growth of microorganisms (Simoncic & Tomsic, 2010).

Finishing chemicals with antimicrobial properties can be divided into two main groups based on their mode of attack on microbes (Schindler & Hauser, 2004). One of them are the chemicals that operate by a controlled-release mechanism (also called leaching antimicrobial), which are the majority of antimicrobial agents used in textile industry (Vigo, 1983). These compounds are not bound to the textile fibers and are effective against the microbes on the fiber surface or in the surrounding environment (Schindler & Hauser, 2004). The second type is the bound antimicrobials, which can be chemically bound to the surfaces of fibers (Schindler & Hauser, 2004).

Products such as copper naphthenate, copper-8-quinolinate, dischlorophene, 3-iodopropynylbutylcarbamate, benzimidazol derivatives, triclosan (2,4,4´-trichloro-2´-hydroxydiphenyl ether), quaternary ammonium slats, organo-silver compounds and silver zeolites belong to the group of controlled-release antimicrobial (Schindler & Hauser, 2004; Payne & Kudner, 1996; Sun & Xu, 1998; Purwar & Joshi, 2004; McDonnell & Russell, 1999; Hermans, 2006; Butkus et al. 2003; Percival et al. 2005; Kim & Sun, 2001; Cai & Sun, 2005). Polyvinylamine and polyvinylformamide (one of its byproducts of synthesis process) are used as flocculants for wastewater

treatment. They are also employed as stabilizers in detergent formulations and personal care products (Niessner et al. 1997). Polyvinylamine are expected to have bacteriostatic or fungicidal effect due to the quaternizable amino. Sustainable Antimicrobial Polymers (SAM polymers) based on vinyl amine derivatives have been developed, specifically for this application (Thölmann et al. 2003).

Using polyamino carboxylic acids for the finishing of cotton is expected to show biostatic properties, too. Table 2.6.11 presents the results of Formazan test of the original cotton and the cotton finished with 1% w/v solution of carboxylated PVAm of different DS values and also the durability of created effect to laundry washing.

Table 2.6.11 Results of the Formazan test as growth inhibition of bacteria (G.I.B) of original cotton (0) and cotton fabric finished with carboxylated PVAm (different DS) and fastness of antibacterial effect after five cycles of laundry washing ($G.I.B_5$)

DS [%]	**G.I.B [%]**	**$G.I.B_5$ [%]**
0	-	-
22.5	90.5	85.7
48.9	81.1	74.2
69.8	65.5	54.2
94.2	55.7	48.6

As it expected carboxylated PVAm creates biostatic properties on cotton. The biostatic property is somehow affected by degree of substitution (DS). The best biostatic effect was obtained when a carboxylated PVAm with the lowest DS (DS 22.5%) was used. The inhibition of bacteria growth was reduced with increasing of DS. The biostatic property depends on the DS value. The effect decrease as the DS value of the PACAs used increases. The biostatic properties are durable to multiple laundry washing.

2.6.8.2 Dyeability of the cotton finished with carboxylated PVAm

Direct and reactive dyes are widely used dyes for dyeing of cotton textiles (Ibrahim et al. 2010). Since reactive dyes can make outstanding brightness of shade, wide color gamut and very good color fastness are the most favored dyes for dyeing of cotton (Lewis & Vo, 2007). Reactive dyes belong to the anionic dyes, in which anionic sulphonate groups (SO_3^-) increase their solubility in water (Lim & Hudson, 2004). Nevertheless, immersing of cotton in water creates negative charges on the surface of fabric resulting in an electrostatic repulsion between the anionic charged hydroxyl groups of cotton and the sulphonate groups of the reactive dyes (Jang et al. 2001). In dyeing mills this problem is practically solved by using a large amount of electrolytes, such as sodium chloride (NaCl) and Glauber salt (Na_2SO_4) to compensate the negative charge of the cotton. The required quantity of salt varies depending on the depth of color and the chemical structure of the dye (Srikulkit & Santifuengkul, 2000). In the last decades environmental concerns in chemical processing of textiles have increased. Therefore, more environmental-friendly processes have been studied and developed to dye the cotton fabrics without or with low amounts of salt (Guan et al. 2007). In this regard the most promising method is the modification of cotton fabric by introducing cationic groups to reduce the negative charge of the surface and therefore reduce or remove the required salt. The efficiency of dyeing is improved by increasing adsorption of dyes on cotton and lowering the waste dyestuff simultaneously (Tutak & Özdemir, 2011). These cationic agents should be permanently fixed on the fabric, commonly through quaternised amino groups (Zhang et al. 2007).

Therefore, it is expected that polyamino carboxylic acids can increase the dyeability of cotton fabrics. The free amino groups of the partially carboxylated polyvinylamine can be protonated and cationize the surface of cotton. Thus, the adsorption of anionic dyes such as reactive dyes should be increased (see Figure 2.6.15).

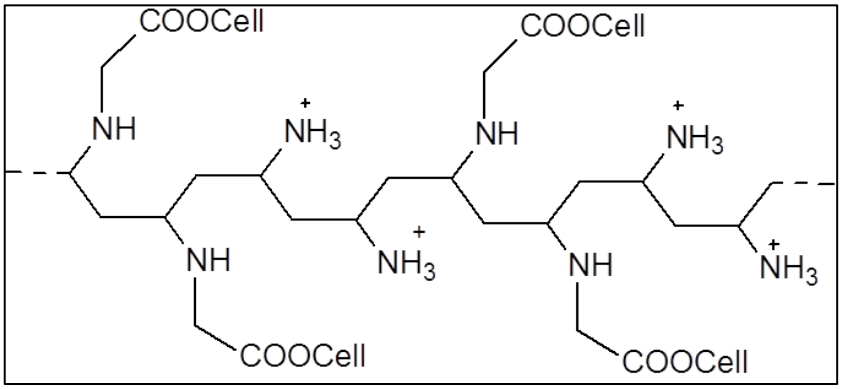

Figure 2.6.15 Fixation of partially carboxylated PVAm with free amino groups on cotton

The finished cotton fabrics with partially carboxylated PVAm (with DS of 54.7% and 69.8%) were dyed with reactive dyes, in presence and absence of salt (sodium chloride). Chemical structures of these dyes are presented in Figure 2.6.16. Figure 2.6.17 shows the K/S values of finished cotton fabrics with partially carboxylated PVAm dyed with Remazol Red RB, Remazol Yellow 3RS and Remazol Brilliant Blue BB, respectively.

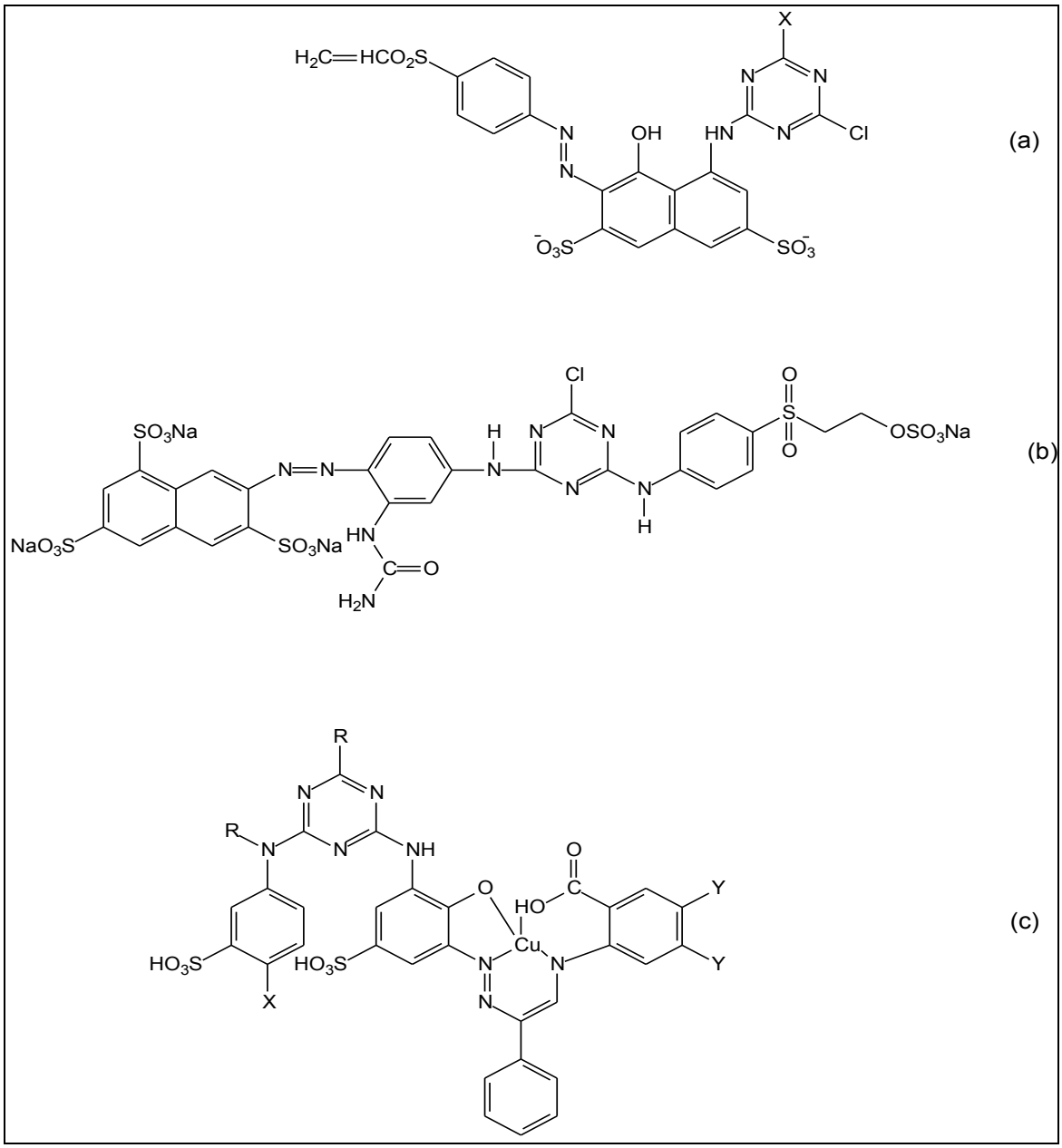

Figure 2.6.16 Chemical structure of Remazol Red RB (a), Remazol Yellow 3RS (b) and Remazol Brilliant Blue BB (c)

The color strength of finished cotton with partially carboxylated PVAm and dyed without salt was much higher than original cotton. On the other hand, the presence of salt in dyeing bath improved the absorbance of reactive dyes to the cotton, so that the color strength of the finished cotton in presence of salt was more than the original cotton dyed under the same conditions.

The color strength of original cotton dyed with reactive dyes and in absence of salt (NaCl) was very low (less than 2). The significant difference in K/S of original cotton dyed in presence of salt in comparison to cotton dyed without salt indicates the necessity of salt for an acceptable dyeing. But when the cotton was finished with partially carboxylated PVAm could adsorb more dye, even in absence of salt. The K/S values of the finished cotton samples for all the used reactive dyes were at least 3 times more than the corresponding original cotton. On the other hand, addition of the salt to dyeing bath of finished cotton could also increase the color strength, which the final K/S of the finished cotton dyed in presence of salt was much higher than the corresponding original cotton. Photos of the original cotton and finished cotton with carboxylated PVAm (different degrees of substitution) and dyed with Remazol Red RB, Remazol Yellow 3RS and Remazol Brilliant Blue BB are presented in Figures 2.6.18, 2.6.19 and 2.6.20, respectively.

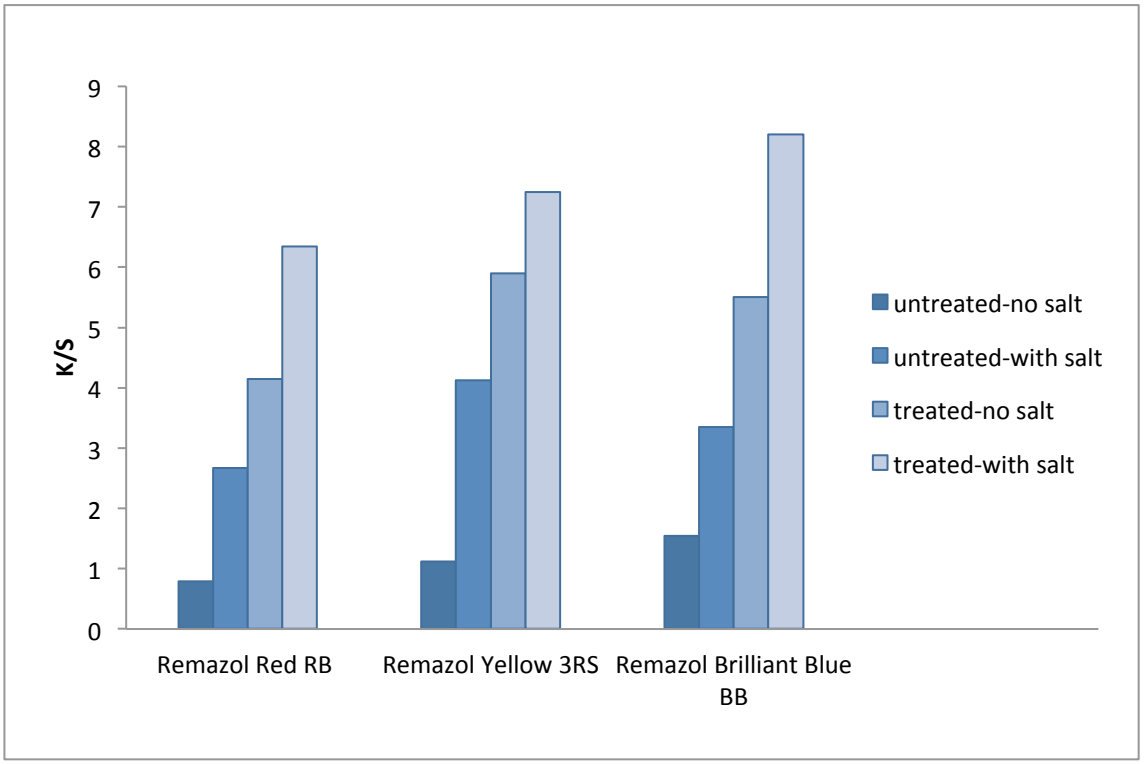

Figure 2.6.17 Color strength (K/S) of original cotton and finished cotton with partially carboxylated PVAm (DS 95.9%) dyed with reactive dyes (2% o.w.f) in presence and absence of salt

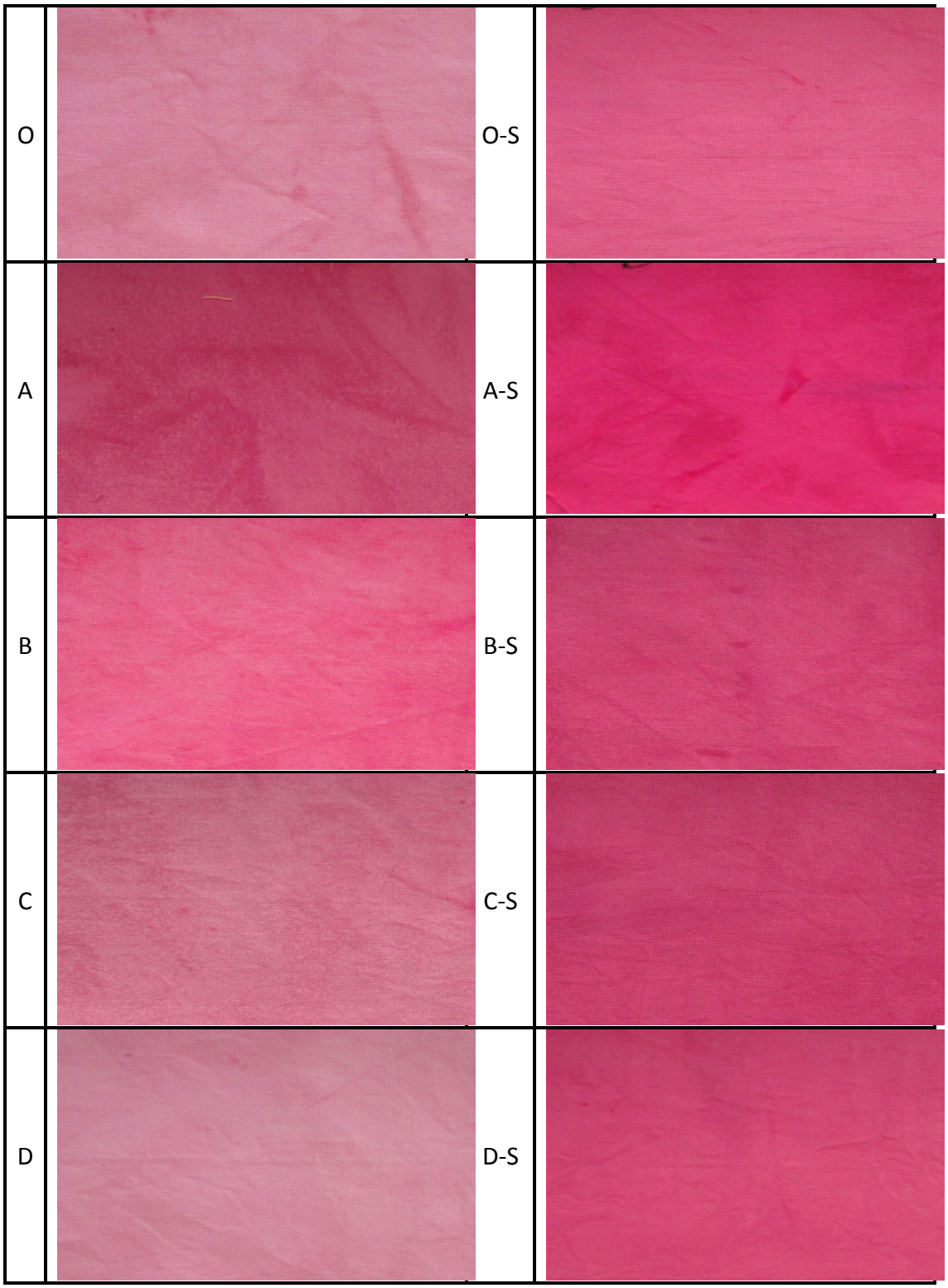

Figure 2.6.18 Photos of cotton dyed with Remazol Red RB in absence of salt: Original (O), finished with carboxylated PVAm-DS 22.4% (A), carb. PVAm-DS 48.6% (B), carb. PVAm-DS 68.8% (C), carb. PVAm-DS 94.6% (D), in presence of salt: original (O-S), finished with carb. PVAm-DS 22.4% (A-S), carb. PVAm-DS 48.6% (B-S), carb. PVAm-DS 68.8% (C-S), carb. PVAm-DS 94.6% (D-S)

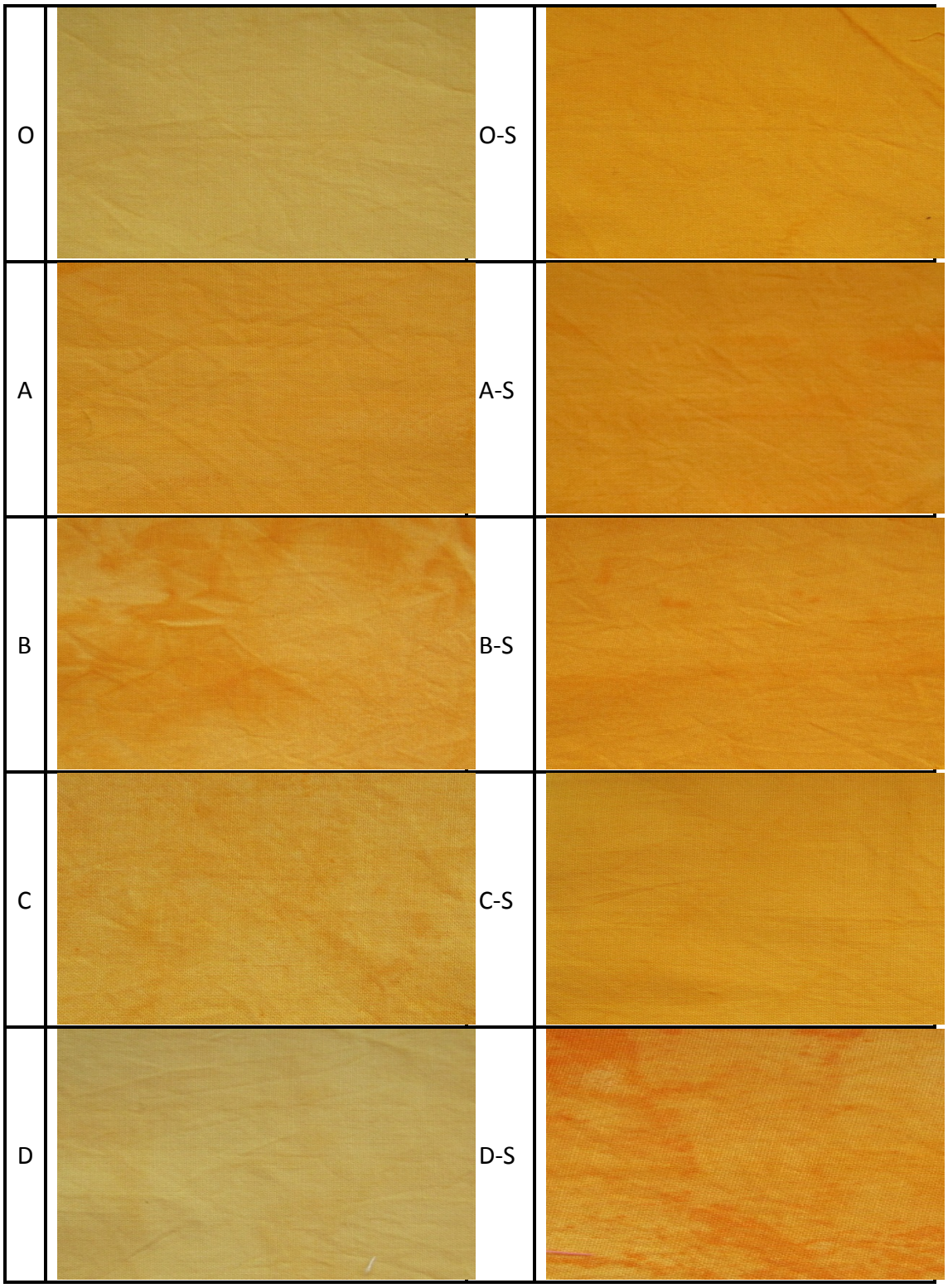

Figure 2.6.19 Photos of cotton dyed with Remazol Yellow 3RS in absence of salt: Original (O), finished with carb. PVAm-DS 22.4% (A), carb. PVAm-DS 48.6% (B), carb. PVAm-DS 68.8% (C), carb. PVAm-DS 94.6% (D), in presence of salt: original (O-S), finished with carb. PVAm-DS 22.4% (A-S), carb. PVAm-DS 48.6% (B-S), carb. PVAm-DS 68.8% (C-S), carb. PVAm-DS 94.6% (D-S)

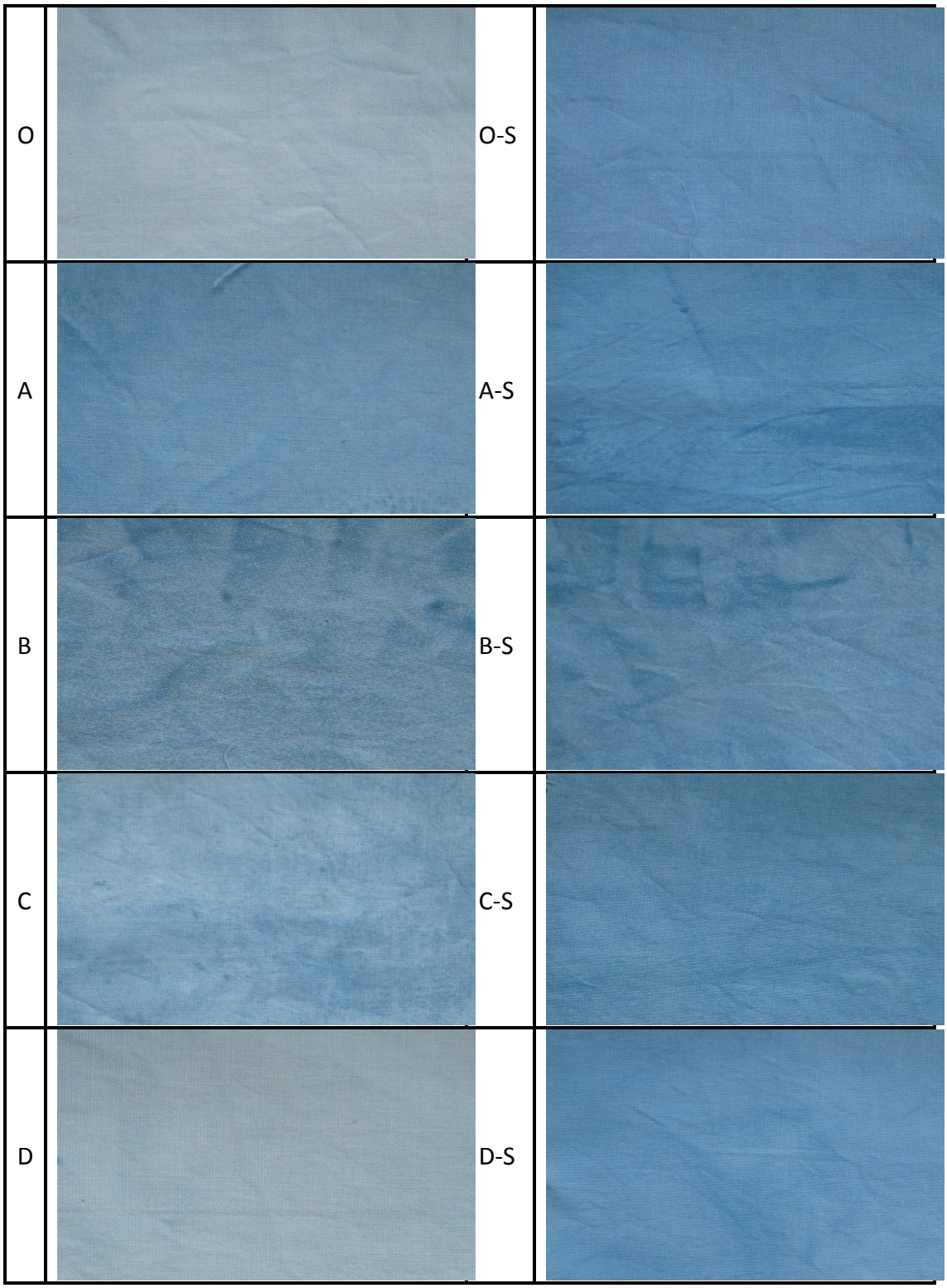

Figure 2.6.20 Photos of cotton dyed with Remazol Brilliant Blue BB in absence of salt: original (O), finished with carb. PVAm-DS 22.4% (A), carb. PVAm-DS 48.6% (B), carb. PVAm-DS 68.8% (C), carb. PVAm-DS 94.6% (D), in presence of salt: original (O-S), finished with carb. PVAm-DS 22.4% (A-S), carb. PVAm-DS 48.6% (B-S), carb. PVAm-DS 68.8% (C-S), carb. PVAm-DS 94.6% (D-S)

Achieving a successful cationic pretreatment of cotton reduces the amount of required amount of salt depending on the number of cationic places introduced to the cotton fabric. Therefore, K/S values of cotton pretreated with PACA depend on the degree of substitution (DS) of PACAs (see Figure 2.6.21). With increasing DS value the number of NH_3^+ – groups decrease and consequently the color strength of the pretreated cotton reduces.

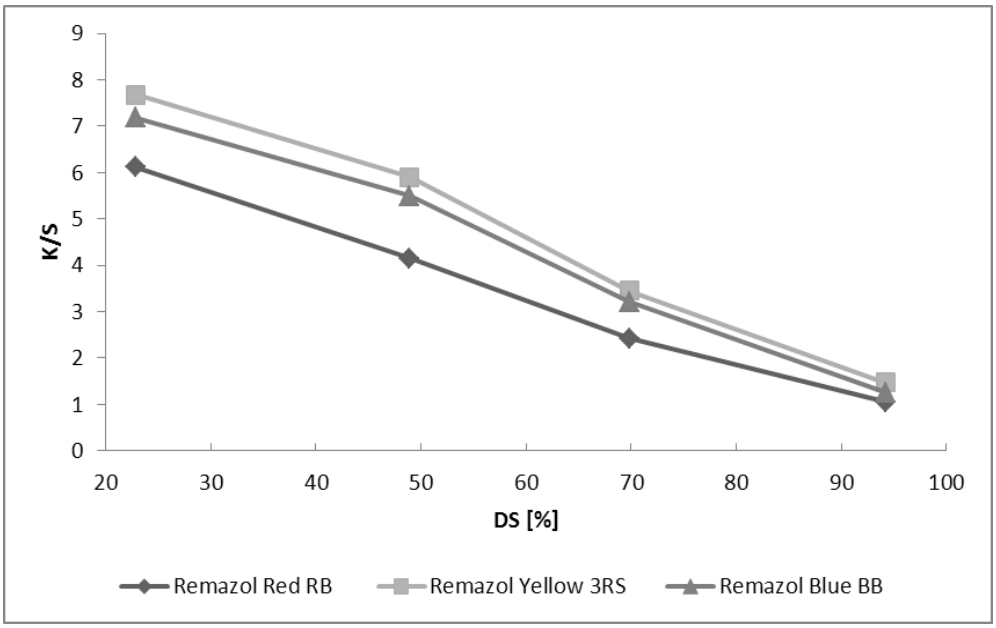

Figure 2.6.21 Changes in K/S values of the cotton pretreated with carboxylated PVAm vs. degree of substitution (DS), dyed with Remazol Red RB, Remazol Yellow 3RS, and Remazol Brilliant Blue BB, 2% o.w.f, in absence of salt

Fastness properties (washing and rubbing fastness) of original and finished cotton with carboxylated PVAm (DS 94.6%), dyed with reactive dyes in absence of electrolyte are presented in Table 2.6.12. The obtained results for all cotton fabrics dyed with reactive dyes indicate that finishing of cotton fabric with partially carboxylated PVAm made almost no negative effect on the fastness properties.

Table 2.6.12 Fastness properties of untreated cotton and cotton pretreated with carboxylated PVAm (DS 69.8%) dyed with reactive dyes, in absence of electrolyte

		Wash fastness	Rubbing fastness	
Dyestuff	Cotton fabrics		Wet	Dry
Remazol Red RB	untreated	5	4-5	5
	pretreated	4-5	4	4-5
Remazol Yellow 3RS	untreated	4-5	4-5	5
	pretreated	4-5	4	4-5
Remazol Brilliant Blue BB	untreated	5	5	4-5
	pretreated	4-5	4-5	4

3

Conclusion and Future Perspectives

3.1 Conclusion

Shortening and simplification of pretreatment and finishing processes in textile industry through combination of two or more stages and application of multifunctional finishing systems are one of the main trends in developing of the textile industry and specially producing of cotton textiles. This demand is originated from the necessity of energy saving, reducing the water consumption and production time.

In pretreatment of cotton fabrics, desizing and acid-demineralization are amongst the most necessary processes, which are usually carried out in separate stages. Acid-demineralization which is used in knitted fabrics has not been yet applied in pretreatment of woven fabric. This is due to that removing cationic metals and alkalis by acid demineralization in woven fabric requires an additional stage, which increases the total cost of production. On the other side, direct application of acid-demineralization for sized cotton is not suggested, because presence of the sizing agent (mainly starch) on warp threads can make an undesirable impact on efficiency of demineralization. Thus, it seems that combination of acid-demineralization with enzymatic desizing can be an alternative way to solve this problem. The relatively new progresses in production of enzymes with more efficiency and less limitation, especially acid-stable starch-converting enzymes, such as α-amylases and glucoamylases enables the users to employ the enzymes in extreme conditions of application. Therefore, the possibility of simultaneous acid-demineralization and enzymatic desizing of cotton fabrics at low pH by use of commercially available glucoamylases and α-amylases and also their mixture, which are relatively active at low pH was investigated in the first part of the present study. By using the mixture of these acid stable enzymes and an appropriate chelating agent at pH 2, a successful desizing of cotton (sized with starch) was achieved at room temperature and also the cationic metals were almost removed. In this way two pretreatment processes could be integrated into a single process. The main advantage of this new method is reducing the time and cost of the process. The practical benefit of this process will be in pretreatment of knitted fabrics, in which

the extra process of acid-demineralization (in conventional method) is not more necessary.

Also in finishing of textiles, the economic benefits, costs, environmental consideration and compatibility of the finishing formulation with other chemicals are the determining factors. The combination of finishing processes in a single bath or at least reducing the number of necessary stages to decrease the costs of production is one of the main demands in textile industry. In this regard, using multifunctional finishing seems as one of the most attractive fields. On the other hand, there is always an increasing demand for those clothes and garments with high specifications and more performances, including easy care garments. Additionally, flammability of textiles is a critical aspect of textiles to ensure the safety of consumers. Protection of consumers from unsafe apparel is one of the areas where flame retardancy is important.

Therefore, in second part of the presented study, a polyamino carboxylic acid was synthesized by reaction of a commercial polyvinylamine and bromoacetic acid. The product of this reaction as a carboxylated polyvinylamine was used for crosslinking of cotton fabric by pad-dry-cure process. The reaction between carboxylic groups of polycarboxylic acid and hydroxyl groups of cellulose in cotton fabric forms ester links, which makes durable press effect in the finished cotton fabric. Presence of more carboxylic groups as functional groups in this new polycarboxylic acid causes better performance in crosslinking of cotton in comparison with conventional polycarboxylic acids. This claim was certified by 60% increase in wrinkle recovery angle of treated cotton and also good fastness of resulted effect against washing. Also whiteness-index and tensile strength of the pretreated cotton were measured. Compared to the conventional polycarboxylic acids (e.g. BTCA), this method showed less side effect on tensile strength and almost whiteness index of finished cotton. Also despite week resistance of ester bonds against hydrolyzing, the durable-press effect in treated cotton showed acceptable wash fastness, which was due to the presence of enough ester bonds in crosslinking net of cotton.

Employment of sodium hypophosphite as a catalyst helped to improvement of ester bonding and reduced the loss of whiteness.

Moreover, the combination of polycarboxylic acid and sodium hypophosphite as a phosphor-containing compound can reduce the flammability of cotton and act as flame retardant agent. The created effect is a function of substitution degree (number of substituted carboxyl groups in PVAm) and the concentration of sodium hypophosphite. The mechanism of flame retardancy by employment of this combination is formation of more non-flammable char and reducing the formation of undesired levoglucosan. The flame retardancy properties of treated cotton with carboxylated PVAm and sodium hypophosphite was proved and certified by 45° flammability test, DSC and measurement of char yield. The created effect was also durable to at least five cycles of laundering washing. However, flame retardancy of cotton by this method caused loss of tensile strength and yellowing of the treated cotton.

Polyvinylamine and partially carboxylated PVAm are expected to have bacteriostatic or fungicidal effect due to the quaternizable amino groups or the substitution reactions of the amine nitrogen in these compounds. Thus, it seems that the treated cotton fabric with carboxylated PVAm should also show biostatic properties. The results of Formazan test certified this claim and indicated that the biostatic properties of treated cotton are depending on the degree of substitution.

Also, the free amino groups in partially carboxylated polyvinylamine can be protonated and cationize the surface of cotton, which can increase adsorption of anionic dyes such as reactive dyes. The presence of free amino groups in these compounds could help to adsorb more reactive dyes through reducing the electrostatic repulsion of dyes and cotton. The K/S values of dyed cottons indicated that by this method, reactive-dyeing of cotton fabrics without electrolyte was also possible. Also fastness properties of dyed samples, including wash fastness and rubbing fastness almost were not affected by the pretreatment process.

3.2 Future Perspectives

Reducing and shortening of necessary stages in chemical pretreatment and finishing of textiles is one of the main trends in development of chemical processing of textiles. For treatment of cotton textiles is combination of process stages even more important, due to the diversity of chemical processes used for cotton fabrics and also the importance of these textiles in world market. The present study has tried to find some ways in order to combine two important chemical pretreatment processes of cotton fabrics and develop a novel finishing method for create several functional effects in cotton fabrics. The first part of study allows the users to combine acid-demineralization and enzymatic desizing of cotton fabric by using acid-stable starch-converting enzymes. It is expected by development of starch-converting enzymes with more stability in acidic conditions, application of these enzymes in sever acidic conditions will be possible and all cationic metals can be simultaneously removed from the cotton fabrics.

The modified cotton with carboxylated polyamines can be a platform for more possibilities in modification of cotton textile. In fact, amine groups in polyamines and polyimines as the functional groups can afford further reactions and consequently more useful derivatives for surface modifications of textiles. Therefore, development of the other finishing effects such as soil-release, water repellency and oil repellency in textiles via introduction of perfluoroalkyl-containing multifunctional groups and providing of medical textiles and cosmetic textiles via introduction of cyclodextrin derivatives into free amine groups of partially carboxylated polyamines and polyimines are possible.

References

"Textilvorbehandlung", A. (1987). *Melliand Textilber, 8*, 581-583.

Altman, F. (1976). Trazolium salts and formazans. *Prog. Histochem. Cytochem., 9*, 1-56.

Andrews, B. (1990). Non-formaldehyde durable press finishing of cotton with citric acid. *Textile Chem. Color., 22*(9), 63-67.

Andrews, B., & Simoneaux, J. (1983). Formaldehyde release and cellulose crosslinking with n-mathylol agents: a delicate balance. *Angew. Macromol. Chem., 115*, 115-117.

Andrews, B., & Trask-Morrell, B. (1991). Esterification crosslinks finishing of cotton fabric with tricarboxylic acids. *Am. Dyest. REp., 80*(7), 26-31.

Andrews, B., Blanchard, E., & Reinhardt, R. (1993). Fabric whiteness retention in durable press finishing with citric acids. *Textile Chem. Color., 25*(3), 52-54.

Andrews, B., Welch, C., & Trask-Morrell, B. (1989). Efficient crosslink finish for formaldehyde-free durable press cotton fabrics. *Am. Dyest. Rep., 78*, 15.

Arami, M., Rahimi, S., Mivehie, L., Mazaheri, F., & Mahmoodi, N. (2007). Degumming of persian silk with mixed proteolytic enzymes. *J. Appl. Polym. Sci., 106*, 267-268.

Arbeitsgruppe Textilvorbehandlung. (1981). Die Violettskala, eine Maßstab für die Beurteilung des Entschlichtungsgrades stärkegeschlichteter Gewebe. *Textilpraxis International, 36*, 1331-1350.

Arumugam, K. (2005). Enzymatic treatment of fibers for nonwovens. *Msc. Thesis*. North Carolina State University, Textile Engineering Department.

Auhorn, W. (1999). Spezialchemikalien für Spezialpapier-Chemikalien zur Erzielun multifunktioneller Eigenschaften. *Wochenblatt für Papierfabrikation, 8*, 505-510.

Bajaj, P. (2002). Finishing of textile materials. *J. App. Polym. Sci., 83*, 631-632.

BASF. (2004). *Polyvinylamin - Eine BASF-Innovation mit Zukunft.* BASF.

Batra, S. (1985). *Handbook of fiber science and technology* (Bd. 4). (M. Lewin, & E. Pearce, Hrsg.) New York: Marcel Deckker.

Battistel, E., Morra, M., & Marinetti, M. (2001). Enzymatic surface modification of acrylonitrile fibers. *Appl. Surf. Sci., 177*, 32-33.

Benitate, J., & Harper , R. (1987). Imparting durable press and flame retardancy to cotton fabrics. *J. Fire. Sci., 5*, 57-69.

Berbner, H. (1990). Eine neue Faser für Schutzkleidung gegen Hitze und Feuer auf Basis Melaminharz. *Chemiefasern/Textilindustrie, 40*(92), 154-157.

Bezwada, R., & Somerville, N. (14. Oct. 1980). *Patentnr. 4,288,045.* United States.

Bhattacharyya, N., Doshi, B., & Sahasrabudhe, A. (2003). Cost effective catalyst for polycarboxylic acid finishing. *Textile Chem. Color., 31*(6), 33-37.

Bishop, D., Shen, J., Heine, E., & Hollfelder, B. (1998). The use of proteolytic enzymes to reduce wool-fiber stiffness and prickle. *J. Textile. Inst., 89*(3), 564-563.

Blanchard, E., & Graves, E. (2002). Polycarboxylic acids for flame resistant cotton/polyester carpeting. *Text. Res. J., 71*(1), 39-43.

Blanchard, E., & Graves, E. (2005). Improving flame resistance of cotton/polyester fleece with phosphorus base polycarboxylic acids. *AATCC Review, 5*(5), 26-30.

Britton, H., & Robinson, R. (1931). Universal buffer solutions and the dissociation constant of Veronal. *J. Chem. Soc.*, 1456-1462.

Brodmann, G. (1990). Performance of nonformaldehyde cellulose reactants. *Textile Chem. Color., 22*(11), 13-16.

Brotherton, D., Fung, K., & Anderson, A. (1989). An alternative zero formaldehyde durable press system. In *Book of papers, 1989 AATCC International Conference* (pp. 170-175). Research Triangel Park, NC: American Assocaiation of Textile Chemists and Colorists.

Brown, R., & Tomasino, C. (1991). Catalysis of 1,2,3,4-butanetetracarboxylic acid in the durable press finishing of cotton. In *Book of Papers, 1991 ATTCC International Conference* (pp. 168-185). Research Triangel Park, NC: American Association of Textile Chemists and Colorists.

Bucheńska, J. (1997). Modified polyacrilonitrile (PAN) fibers. *J. Appl. Polym. Sci., 65*, 1955-1996.

Buleon, A., Colonna, P., Planchot, V., & Ball, S. (1998). Starch granules: structure and biosynthesis. *Int. J. Bopl. Macromol. , 23*, 85-88.

Buschle-Diller, G., El Mogahzy , Y., Inglesby, M., & Zeronian, S. (1998). Effects of scouring with enzymes, organic solvents, and caustic soda on the properties of hydrogen peroxide bleached cotton yarn. *Text. Res. J. , 68*(3), 920.

Buschle-Diller, G., Yang, X., & Yamamoto, R. (2001). Enzymatic bleaching of cotton with glucose oxidase. *Text. Res. J. , 71*(5), 388.

Butkus, M., Edling, L., & Labare, M. (2003). The efficacy of silver as a bactericidial agent: advantages, limitations and considerations for future use. *J. Water Sup. Res. Tech.-Aqua, 52*, 407-416.

Cai, Z., & Sun, G. (2005). Antimicrobial finishing of acrilan fabrics with cetylpyridinium chloride: affected properties and structures. *J. Appl. Polym. Sci., 97*, 1227-1236.

Cavaco- Paulo, A., & Gübitz, G. (2003). *Textile processing with enzymes.* Boca Raton: CRC Press.

Cavaco-Paulo, A. (1998). Processing textile fibers with enzymes: an overview. *ACS Symposium Series*, *687*, S. 180-189.

Cavaco-Paulo, A. (1999). Laccases for textile applications. *217th Am. Chem. Soc., National Meeting*, (S. 21-25). Anheim, CA,.

Chance, L., Danna, G., & Andrews, B. (1990, Feb 13). *Patent No. 4,900,324.* United States.

Chao, T., & Somerville, N. (1973, Sep. 2). *Patent No. 3,903,033.* United States.

Chen, C., & Wang, C. (2006). Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nano-catalyst under UV irradiation. *J. Sol-gel. Sci. Tech., 40*(1), 31-38.

Chen, D., Yang, C., & Qiu, X. (2005). Aqueous polymerization of maleic acid and crosslinking of cotton cellulose by the poly(maleic acid). *Ind. Eng. Chem. Res., 44*, 7921-7927.

Cheng, X., & Yang, C. (2009a). Flame retardant finishing of cotton fleece fabric: Part V. Phosphorus-containing maleic acid oligomers. *Fire. Mat., 33*, 365-375.

Cheng, X., & Yang, C. (2009b). Flame retardant finishing of cotton fleece fabric: Part VI. The combination of a hydroxyl-functional organophosphorus oligomer and 1,2,3,4-butanetetracarboxylic acid. *J. Fire. Sci., 27*, 583-600.

Chikkodi, S. V., Khan, S., & Mehta, R. D. (1995). Effects of biofinishing on cotton/wool blended fabrics. *Text. Res. J., 65*(10), 563-569.

Chikkodi, S., Khan, S., & Mehta, R. (1995). Effects of biofinishing on cotton /wool blended fabrics. *Text. Res. J. , 65*, 564-569.

Choi, H., & Kim, Y. (2001). Performance improvement of nonformaldehyde wrinkle resistant finished cotton fabrics treated with dialdehydes. *Fiber Polym, 2*(4), 190-195.

Choi, H., & Welch, C. (1992). Unsaturated dicarboxylic acids in nonformaldehyde DP finishing of cotton. In *Book of papers, 1992 AATCC International Conference* (pp. 287-293). Atlanta, GA: American Association of Textile Chemists and Colorists.

Choi, H., Welch, C., & Morris, N. (1993). Nonphosphorus catalysts for formaldehyde-free DP finishing of cotton with 1,2,3,4-butanetetracarboxylic acid. *Text. Res. J., 63*(11), 650-657.

Chung, Y., Lee, K., & Kim, J. (1998). Durable press and antimicrobial finishing of cotton fabrics with a citric acid and chitosan treatment. *Textile. R. J., 68*(10), 772-775.

Cole, R. (7. March 1978). *Patentnr. 4,078,101.* United states.

Colonna, S., Gaeggero, N., Richelmi, C., & Pasta, P. (1999). Recent biotechnological developments in the use of peroxidases. *Tibtech, 17*, 163-168.

Copeland, R. (2001). *Enzymes: biochemistry and biotechnology.* Chichester: Clinical Chemistry, Horwood Publishing.

Costa, S., Tzanov, T., Paar, A., Gudelj, M., Gübitz, G., & Cavaco-Paulo, A. (2001). Immobilization of catalases from Bacillus SF on alumina for the treatment of textile bleaching effluents. *Enzyme Microb. Tech., 28*, 815-819.

Coutinho, P., & Reilly, P. (1997). Glucoamylase structural, functional, and evolutionary relationships. *Proteins: Struct. Funct. Genet., 29*, 333-347.

Cox, T. (2005). Intumescent barrier finishes for textiles. *AATCC Reviews*, 38-39.

Csiszár, E., Szakács, G., & Rusznák, I. (1998). Combining traditional cotton scouring with enzymatic treatment. *Text. Res. J. , 68*(3), 163.

Das, T., & Ramaswamy, G. (2006). Enzyme treatment of wool and specialty hair fibers. *Text. Res. J. , 76*(2), 126-127.

Dastjerdi, R., Montazer, M., & Shahsavan, S. (2010). A novel technique for producing durable multifunctional textiles using nanocomposite coating. *Colloids. Surf., 81*, 32-41.

De, P. (1998). Denim washing and finishing: a review. *Man-made Text. India, 41*(3), 129-131.

Dermeik, S., Braun, R., & Lemmer, K. (2006, Jan 3). *Patent No. 6,981,998.* United States.

Diderichsen, B. (1995). A new desizing enzyme shows the changing nature of enzyme production. *J. Biotechnol., 38*, 196.

Dombrowski, R. (2002). Intumescent barrier coatings. *Proc. AATCC*, 55-62.

Donelli, I., Taddei, P., Smet, P., Poelman, D., Nierstrasz, V., & Freddi, G. (2009). Enzymatic surface modification and functionalization of PET: a water contact angle, FTIR, and fluorescence spectroscopy study. *Biotech. Bioeng. , 103*(5), 845-847.

Dring, I. (2003). Anti-microbial, rotproofing and hygiene finishes. In D. Heywood, *Textile Finishing* (pp. 351-357). Bradford: Society of Dyers and Colourists.

Durán, N., & Duráa´n, M. (2000). Enzyme applications in the textile industry. *Rev. Prog. Coloration., 30*, 41-42.

Etters, J., Husain, P., & Lange, N. (1995). Alkaline pectinase: an ecofriendly approach to cotton preparation. *Textile Asia, 5*(83), 5.

(2008). Polymer additives: plasticizers and flame retardants. In B. Fahlman, *Materials Chemistry* (pp. 264-269). Dordrecht: Springer.

Feitkenhauer, H., Fischer, D., & Fäh, D. (2003). Microbial desizing using starch as model compound: Enzyme properties and desizing efficiency. *Biotechnol. Prog.*(19), 847-848.

Festel, G., Knöll, J., Götz, H., & Zinke, H. (2004). Der Einfluss der Biotechnologie auf Produktionsverfahren in der Chemieindustrie. *Chemie Ingenieur Technik, 76*, 307-312.

Frank, A., Daigle, D., & Vail, S. (1982). Chemistry of hydroxymethyl phosphorus compounds. Part II: Phosphonium salts. *Text. Res. J., 52*, 678-693.

Frick, J., & Happer, R. (1984). Acetals as crosslinking reagents for cotton. *J. Appl. Polym. Sci., 29*, 1433-1447.

Frick, J., & Harper, R. (1981). Adducts of glyoxal and amides as finishing agents for cotton. *Text. Res. J., 51*, 601-606.

Frick, J., & Harper, R. (1982). Investigations toward formaldehyde-free finishes. *Text. Res. J., 52*, 141-148.

Fujii, M., & Kawamura, Y. (1985). Synergistic action of α-amylase and glucoamylase on hydrolysis of starch. *Biotechnol Bioeng., 27*(30), 260.

Fukuda, T., Kato-Murai, M., Kuroda, K., & Ueda-Shin-ichiro Suye, M. (2008). Improvement in enzymatic desizing of starched cotton cloth using yeast codisplaying glucoamylase and cellulose-binding domain. *Appl Microbiol Biotechnol.*(77), 1225.

Gaan, S., & Sun, G. (2007a). Effect of phosphorus and nitrogen on flame retardant cellulose: a study of phosphorus compounds. *J. Anal. Appl. Pyrol., 78*, 371-379.

Gaan, S., & Sun, G. (2007b). Effect of phosphorus flame retardants on thermo-oxidative decomposition of cotton. *Polym. Degrad. Stab., 92*, 968-974.

Gaan, S., & Sun, G. (2009). Effect of nitrogen additives on thermal decomposition of cotton. *J. Anal. Appl. Pyrol., 84*, 108-115.

Garland, C. (1993). Colour Technology. In C. Gultekin, *Textile Chemistry* (S. 107). Research Triangle Park: American Association of Textile Chemists and Colorists.

Garratt, R., & Grishham, C. (1999). *Biochemistry* (2nd Edition ed.). New York: Saunders College Publishing.

Geubtner, M. (1990). Fortschritte bei der Hochveredlung von Viskose-und Modalfaserartikeln. *Melliand Textilberichte, 7*, 214-218.

Gillingham, E., Lewis, D., & Voncina, B. (1999). An FTIR study of anhydride formation on heating butane tetracarboxylic acid in the presence of various catalysts. *Text. Res. J., 69*(12), 949-955.

Gonzales, E., & Benerito, R. (1965). Effect of the catalyst upon the physical and chemical properties of cotton cellulose finished wit derivatives of ethyleneurea. *Text. Res. J., 35*, 168-177.

Gu, X., & Yang, C. (2000). FTIR Spectroscopy of the formation of cyclic anhydride intermediates of polycarboxylic acids catalyzed by sodium hypophosphite. *Text. Res. J., 70*(1), 64-70.

Guan, Y., Zheng, Q., Mao, Y., Gui, M., & Fu, H. (2007). Application of polycarboxylic acid sodium salt in the syeing of cotton fabric with reactive dyes. *J. Appl. Polym. Sci., 105*, 726-732.

Gübitz, G., & Cavaco-Paulo, A. (2003). New substrates for reliable enzymes: enzymatic modification of polymers. *Curr. Opion. Biotech., 14*, 577-582.

Gübitz, G., & Cavaco-Paulo, A. (2007). Enzymes go big: surface hydrolysis and functionalisation of synthetic fibers. *Tibiotec, 26*, 32-36.

Gudelj, M., Fruhwirth, G., Paar , A., Lottspeich, F., Robra, K., & Cacaco-Paulo, A. (2001). A catalase-peroxidase from a newly isolated thermokaliphilik Bacillus sp. with potential for the treatment of textile bleaching effluents. *Extremophiles, 5*(6), 423-429.

Harper, R., & Frick, J. (1981). Increasing the effectiveness of formaldehyde-free finishing agent. *Amer. Dyest. Reptr., 70*(9), 46-76.

Hashem, M. M. (2007). An approach to a single pretreatment recipe for different types of cotton. *Fibers Text. East. Eur. , 15*(2), 85.

Hebeish, A., Hashem, M., & Higazy, A. (2001). A new method for preventing catalytic degradation of cotton cellulose by ferrous or ferric ions during bleaching with hydrogen peroxide. *Macromol. Chem. Phys., 202*(6), 949-650.

Hebeish, A., Waly, A., El-Aref, A., Abdel-Mohdy, F., & Zamzam, N. (1994). Behaviour of chemically modified cottons towards flame-retradancy finishing. *Polym. Deg. Stab., 43*, 447-459.

Heng, C., Chen, Z., Du,, L., & Lu, F. (2005). Expression and secretion of an acid-stable alpha-amylase in bacillus subtilis by SacB promoter and signal peptide. *Biotechnol. Lett., 27*, 1731-1732.

Hermans, M. (2006). Silver-containing dressings and the need for evidence. *Am. J. Nurs, 106*, 60-68.

Horrocks, A. (1983). An introduction to the burning behaviour of cellulosic fibers. *JSDC, 99*, 191.

Horrocks, A. (1986). Flame retardant finishing of textiles. *Rev. Prog. Color., 16*, 62-101.

Horrocks, A. (1996). Developments in flame retardants for heat and fire resistant textiles. *Polym. Degrad. Stab., 54*, 143-154.

Horrocks, A. (2003). Flame-retardant finishes and finishing. In D. Heywood, *Textile Finishing* (pp. 214-250). Bradford: Society of Dyers and Colourists.

Horrocks, A., & Price, D. (2000). *Fire retardant materials.* Cambridge: Woodhead publishing .

Horton, H., Moran, L. A., Gray Scrimgeour, K., Perry, M. D., & Rawn, J. D. (2006). *Principles of biochemistry* (4th edition ed.). New Jersey: Pearson Education, Inc.

Hsieh, Y., Thompson, J., & Miller, A. (1996). Water wetting and retention properties of cotton assemblies as affected by alkaline and bleaching treatments. *Text. Res. J. , 66*, 456-464.

Hvattum, O., & Turner, H. (1951). The removal of impurities from grey cotton, Part I – A review of developments in plant for alkali boiling. *JSDC, 67*(11), 416-424.

Ibrahim, N., Abo-Shosh, M., Elnagdy, E., & Gaffar, M. (2002). Eco-friendly durable press finishing of cellulose-containing fabrics. *J. Appl. Polym. Sci., 84*, 2243-2253.

Ibrahim, N., El. Hossamy, M., Morsy, M., & Eid, B. (2004). Development of new eco-friendly options for cotton wet processing. *J. Appl. Polym. Sci., 93*, 1825.

Ibrahim, N., Mahrous, F., El-Gamal, A., Gouda, M., & Husseiny, S. (2010). Multifunctional Anionic Cotton Dyeings. *J. Appl. Polym. Sci., 115*, 3249-3255.

Illanes, A. (2008). *Enzyme biocatalysis, principles and applications.* Springer.

Imamura, Y., Nagatomo, E., Serizawa, T., Muraoka, Y., Akashi, M., & Yamamoto, K. (2003). Synthesis and functionalities of poly(N-alkylamide). XIV. Polyvinylamine produced by hydrolysis of poly(n-vinylformamide) and its functionalization. *J. Appl. Polym. Sci., 89*, 1277-1283.

Jang, J., Ko, S., & Carr, C. (2001). Investigation of the improved dyeability of cationised cotton via photografting with UV active cationic monomers. *Color. Technol., 117*, 139-146.

Jovancic, P., Jocic, D., & Dumic, J. (1998). The efficiency of an enzyme treatment in reducing wool shrinkage. *J. Textile. Inst., 89*(2), 390-392.

Kadolph, S., & Langford, L. (2001). *Textiles.* NJ: Prentice Hall.

Kandola, B., & Horrocks, A. (2000). Complex char formation in flame-retarded intumescent combinations. *Fire Mater, 24*, 265-275.

Kandola, B., Horrocks, A., Price, D., & Coleman, G. (1996). Flame retardant treatments of cellulose and their influence on the mechanism of cellulose pyrolysis. *J. Macromol. Sci. -Rev. Macromol. Chem. Phys., C36*(4), 721-724.

Karmakar, S. (1999). *Textile science and technology, chemical technology in the pre-treatment of textiles* (Bd. 12). New York: El Sevier.

Kelkar, H., & Deshpande, M. (1993). Purification and charactrization of a pullulan-hydrolyzing glucoamylase from Sclerotium rolfsii. *Starch-Staerke, 45*, 361-368.

Kim, B., Jang, J., & Ko, S. (2000). Durable press finish of cotton fabric using maleic acid as a crosslinker. *Fiber Polym, 1*(2), 116-211.

Kim, Y., & Sun, G. (2001). DDurable antimicrobial finishing of nylon fabrics with acid dyes and a quaternary ammonium salt. *Text. Res. J., 71*, 318-323.

Kittinaovarat, S., Kantuptim, P., & Singhaboonponb, T. (2006). Wrinkle resistant properties and antimicrobial efficacy of cotton fabrics treated with glyoxal system and with combination of glyoxal and chitosan system. *J. Appl. Polym. Sci., 100*, 1372-1377.

Kiumarsi, A., & Parvinzadeh, M. (2010). Enzymatic hydrolysis of nylon 6 fiber using lipolytic enzyme. *J. Appl. Polym. Sci. , 116*, 3140-3146.

Klemm, D., Phillip, B., Heinze, U., & Wagenknecht, W. (1998). *Comprehensive Cellulose Chemistry. Vol I. Fundamentals and Analytical Methods.* Weinheim: Wiley-VCH Verlag GmbH.

Klun, U., Friedrich, J., & Kran, A. (2003). Polyamide – 6 fiber degradation by lignolytic fungus. *Polym. Deg. Stab, 79*, 99.

Klyosov, A. A. (1990). Trends in biochemistry and enzymology of cellulose degradation. *Biochemistry, 29*(47), 10577-10588.

Kobayashi, M., & Shimizu, S. (1994). Versatile nitrilases: nitrile-hydrolyzing enzymes. *FEMS Microbiol. Lett., 120*, 217-224.

Kokot, S., & Jermini, M. (1994a). Characterizing oxidatively damaged cotton fabrics: Part I: A method for estimating relative fabric damage. *Text. Res. J., 64*(2), 100.

Kokot, S., Marahusin, L., Schweinsberg, D., & Jermini, M. (1994b). Characterizing oxidatively damaged cotton fabrics: Part II: A model for the catalytic damage phenomenon using electrogenerated oxygen. *Text. Res. J., 64*(12), 710.

Koo, H., Ueda, M., Yoshimura, T., & Igarashi, T. (1994). Cellulase treatment of cotton fabrics. *Text. Res. J. , 64*, 70-74.

Krassig, H. (1985). *Structure of cellulose and its relation to properties of cellulose fibers, cellulose and its derivatives, chemistry, biochemistry and applications.* West Sussex: Ellis Hardwood Limited.

Lacasse, K., & Baumann, W. (2004). *Textile chemicals: environmental data and facts.* Berlin: Springer.

Lam, Y., Kan, C., & Yuen , C. (2010). Effect of concentration of titanium dioxide acting as catalyst on the wrinkle-resistant finishing of cotton fabric. *Fiber Polym, 11*(4), 551.

Lam, Y., Kan, C., & Yuen, C. (2011). Wrinkle-resistant finishing of cotton fabric with BTCA-the effect of co-catalyst. *Text. Res. J., 81*(5), 482-493.

Lammermann, D. (1992). New possibilities for non-formaldehyde finishing of cellulosic fibers. *Melliand Textilber, 3*, 274-279.

Lancaster, M. (2002). *Green chemistry: An introductory text.* New York: The Royal Society of Chemistry, University of New York.

Lantto, R., Schönberg, C., & Buchert, J. (2004). Effects of laccase-mediator combinations on wool. *Text. Res. J. , 74*(8), 713.

Lecoeur, E., Vorman, I., Bourbigot, S., Lam, T., & Delobel, R. (2001). Flame retardant formulations for cotton. *Polym. Degrad. Stab., 74*, 487-493.

Lee, E., & Kim, S. (2004). Effect of glycols and catalysts on cotton fabrics treated with glyoxal. *Fiber Polym, 5*(3), 230-233.

Lessan, F., Montazer, M., & Moghadam, M. (2011). A novel durable flame-retardant cotton fabric using sodium hypophosphite, nano TiO2 and maleic acid. *Thermochim. Acta, 520*, 48-54.

Levin, M. (1983). *Handbook of fiber science and technology: Voll. II. Chemical processing of fibers and fabrics.* New York: Marcel Dekker.

Lewis, D., & Vo, L. (2007). Dyeing Cotton with Reactive Dyes under Neutral Conditions. *Color. Technol., 123*, 306-311.

Lewis, D., & Voncina, B. (1997a). Durable press finishing of cotton with polycarboxylic acids. I. Preparation of thiosuccinyl-s-triazine. *J. Appl. Polym. Sci., 66*, 1465-1474.

Lewis, D., & Voncina, B. (1997b). Durable press finishing of cotton with polycarboxylic acids. II. Ester crosslinking of cotton with dithiosuccinic acid derivative of S-triazine. *J. Appl. Polym. Sci., 66*, 171-177.

Lim, S., & Hudson, S. (2004). Application of a fibre-reactive chitosan derivative to cotton Fabric as a zero-salt dyeing auxiliary. *Color. Technol., 120*, 108-113.

Lu, Y., & Yang, C. (1999). Fabric yellowing caused by citric acid as a crooslinking agent for cotton. *Text. Res. J., 69*(9), 685-690.

Maarel, M. J. (2009). *Starch-Processing Enzymes, in Enzymes in Food Technology* (Second edition Ausg.). Oxford: Wiley-Blackwell.

Martel, B., Morcellet, M., Ruffin, D., & Weltrowski, M. (2002). Finishing of polyester fabrics with cyclodextrins and polycarboxylic acid as crosslinking agents. *J. Inclusion Phenom. Macrocyclic Chem., 44*, 443-446.

Martel, B., Weltrowski, M., Ruffin, D., & Morcellet, M. (2000). Polycarboxylic acids as crosslinking agents for grafting cyclodextrins onto cotton and wool fabrics: study of the process parameters. *J. Appl. Polym. Sci., 83*, 1449-1456.

Matamá, T., Carneiro, F., Gübitz, G., & Cavaco-Paulo, A. (2007). Using a nitrilase for the surface modification of acrylic fibers. *Biotechnol. J.*, 353-354.

McCall, E., & Jurgens, J. (1951). Chemical composition of cotton. *Text. Res. J. , 21*(1), 19-21.

McDonnell, G., & Russell, A. (1999). Antiseptics and disinfectants: activity, action and resistance. *Clin. Mirobiol. Rev., 12*, 147-179.

McKerron, C. (1987). Focuses on formaldehyde. *Chem. Week., 140*, 15.

Meyer, U., Kokot, S., Weber, R., & Zürcher, J. (1987). What is catalytic damage? Try to explain the mechanism. *Textilveredlung*(22), 185-190.

Meyers, R. A. (2011). *Encyclopedia of analytical chemistry: applications, theory, and instrumentation.* John Wiley & Sons.

Mori, T., Sakimoto, M., & Kagi, T. (1997). Enzymatic desizing of polyvinylalcohol from cotton fabrics. *J Chem Technol Biotechnol.*(68), 151.

Morris, C., Morris, N., & Trask-Morrell, B. (1996). Interaction of meso-butanetetracarboxylic acid with phosphorus containing catalysts for esterification crosslinking-linkage of cellulose. *Ind. Eng. Chem. Res., 35*, 950-953.

Niessner, M., Nilz, C., Hössel, P., Kothrade, S., & Sanner, A. (1997, Sep 29). *Patent No. 0929285.* EP.

Nolte, H., & Bishop, D. (1996). Effects of proteolytic and lipolytic enzymes on untreated and shrink-resist-treated wool. *J. Textile. Ins., 87*(1), 212-226.

Oppermann, W., Gutmann, R., Schmidt, S., & Held-Föhn, E. (2003). Schnelltest zur Beurtailung antimikrobieller Textilien. *Textilveredlung, 37*, 16-21.

Opwis, K., Knittel, D., & Schollmeyer, E. (2007). Functionalization of catalase for a photochemical immobilization on poly(ethylene terphtalate). *Biotechnol. J., 2*, 347.

Opwis, K., Knittel, D., Kelle, A., & Schollmeyer, E. (1999). Enzymatic recycling of starch – containing desizing liquors. *Starch/Stärke, 51*(10), 348.

Parvinzadeh, M. (2009). A new approach to improve dyeability of nylon 6 fiber using a subtilisin enzyme. *Color. Technol., 125*(4), 228-233.

Payne, J., & Kudner, D. (1996). A durable anti-odor finish for cotton textiles. *Textile Chem. Color., 28*(5), 28-30.

Percival, S., Bowler, P., & Russell, D. (2005). Bacterial resistance to silver in wound care. *J. Hosp. Infect., 6*, 1-7.

Perkins, R., Drake, G., & Reeves, W. (1966). DTA and TGA studies of flame resistant fabrics. *J. Appl. Polym. Sci.* , 1041-1066.

Philippidis, G. (1994). Cellulase production technology, evaluation of current status, in enzymatic conversion of biomass for fuels production. *ACS Symposium Series. 566*, S. 188-217. Washington DC: Am. Chem. Soc.

Presa, P., & Tavcer, P. (2009). Low water and energy saving process for cotton pretreatment. *Text. Res. J., 79*(1), 77.

Purwar, R., & Joshi, M. (2004). Recent developments in antimicrobial finishing of textiles-A review. *AATCC REv., 4*, 22-26.

Qing, F., Ja, M., Yan, K., & Mao, Z. (2002). Synthesis of perfluroalkyl-containing multifunctional groups compounds for textile finishing. *J. Flour. Chem, 113*, 139-141.

Quand, C., & Kühl, B. (2000). Einsatzmöglichkeiten und Optimierung enzymatischer Prozesse in der Textilveredlung. *Melliand Textilberichte*, 834-836.

Renz, W., Carroll, W., Yacoub, K., Drescher, J., Nordquist, A., Cheng, N., et al. (1997). N-vinylformamide-building block for novel polymer structures. *Pure Appl. Chem., A34*, 1885-1905.

Robner, U. (1993). Enzymatic degradation of impurities in cotton. *Melliand Textilberichte, 74*, 63.

Roles, J., & Delft, T. (1979). Kinetics of reactions with amyloglucosidase and their relevance to industrial applications. *Starch-Staerke, 31*(10), 338.

Rouette, H. (2001). *Encyclopedia of textile finishing.* Springer.

Rousselle, M., Bertoniere , N., Howley, S., & Wgoynes, W. (2002). Effect of whole cellulase on the supramolecular structure of cotton cellulose. *Text. Res. J. , 72*(11), 963-972.

Rowland, S., Welch, C., Brannan, A., & Galagher, D. (1967). Introduction of ester cross-links into cotton cellulose by a rapid curing process. *Text. Res. J., 37*, 933-941.

Sauperl, O., Santa-Kleinschek, K., & Ribitsch, V. (2009). Cotton cellulose 1,2,3,4 buthanetetracarboxylic acid (BTCA) crosslinking monitored by some physical-chemical methods. *Text. Res. J., 79*(9), 780-791.

Schao-Wei, D., & Da-Nian, L. (2008). Kinetics of the thermal inactivation of bacillus subtilis α-amylase and its application on the desizing of cotton fabrics. *J. App. Poly. Sci, 109*, 3733.

Schick, M. (1975). *Surface characteristics of fibers and textiles, Part I.* New York: Marcel Dekker Inc.

Schindler, W., & Hauser, P. (2004). *Chemical finishing of textiles.* Boca Raton: CRC Press.

Schönbergr, H., & Schäfer, T. (2003). *Best available techniques in textile industry.* Berlin: Federal Environmental Agency (Umweltbundesamt).

Schramm, C., Rindered, B., & Bobleter, O. (1998). Quantitative determination of BTCA bound to cellulosic material by means of isocratic HPLC. *Text. Res. J., 68*(11), 821.

Schröder, W. (1994). Poly(amine). In *Methoden der organischen Chemie* (Bd. E20/2). Stuttgart: Thiemen Verlag.

Segal, L., & Timpa, J. (1973). Strength losses and structural changes in cotton fabric crosslinked with dimethylolethylenurea. *Text. Res. J., 43*, 185.

Shahin, U., Gursoy, N., Hauser, P., & Smith, B. (2009). Optimization of ionic crosslinking process: an alternative to conventional durable press finishing. *Text. Res. J., 79*(8), 744.

Sharpe, G., & Mallinson, P. (2003). Easy care finishing of celluolsics. In D. Heywood, *Textile finishing* (pp. 337-350). Society of Dyers and Colourists.

Shuler, M., & Kargi, F. (2002). *Bioprocess engineering basic concepts* (Second Edition Ausg.). Prentice Hall.

Silva, C., & Cavaco-Paulo, A. (2004). Monitoring biotransformations in polyamide fibers. *Biocatal. Biotrans., 22*, 357.

Simoncic, B., & Tomsic, B. (2010). S tructures of novel antimicrobial agents for textiles - A review. *Text. Res. J., 80*(16), 1721-1737.

Singh, R., Sharma, R., & Rawat, G. D. (2006). Nitrilase and its application as a green catalyst. *Chem. Biodivers. , 3*, 1279-1285.

Sircharussin, W., Ryo-Aree, W., Intasen, W., & Poungraksakirt, S. (2004). Effect of boric acid and BTCA on tensile strength loss of finished cotton fabrics. *Text. Res. J., 74*(6), 475-480.

Siva, C. M., Caneiro, F., O'Niell, A., Fonesca, L., Cabral, J. S., Gübitz, G., et al. (2005). Cutinase – a new tool for biomodification of synthetic fibers. *J. Polym. Sci., 43*, 2448-2450.

Srikulkit, K., & Santifuengkul, P. (2000). Salt-free dyeing of cotton cellulose with a model cationic reactive dye. *J.S.D.C., 116*, 398-402.

Stewart, M. A. (2005). Biopolishing cellulosic nonwovens. *PhD Dissertation*. North Carolina State University.

Sun, G., & Xu, X. (1998). Durable and regenerable anti-bacterial finishing of fabrics: biocidal properties. *Textile Chem. Color., 30*(6), 26-30.

Tauber, M., Cavaco-Paulo, A., Robra, K., & Gübitz, G. (2000). Nitrile hydratase and amidase from rhodococcus rhodochrous hydrolyze acrylic fibers and granular polyacrylonitrlies. *Appl. Environ. Microbiol., 66*(4), 1634.

Tester, R., Karkalas, J., & Qi, X. (2004). Starch-composition, fine structure and architecture. *J. Cereal. Sci. , 39*, 151-154.

Thölmann, D., Kossmann, R., & Sosna, F. (2003). SAM-Polymers-ein polymerbiozides Additiv (Polymers with antimicrobial properties). *Europ. Coating. J.* , 105-107.

Tomasino, C. (1992). *Chemistry and technology of fabric preparation and finishing.* Raleigh NC: North Carolina State University, College of Textiles.

Trask-Morrell, B., & Andrews, B. (1992). Thermoanalytical ranking of catalysts for use with polycarboxylic acids as durable press reactants. *Text. Res. J., 62*, 144.

Trask-Morrell, B., Kottes Andrews, B., & Graves, E. (1990). Spectrometric analysis of polycarboxylic acids. *Textile Chem. Color., 22*(10), 23.

Trieselt, W. (1970). The Chemistry of damage in peroxide bleaching (in German). *Melliand Textilber*(51), 1094-1097.

Trotman, E. R. (1970). *Dyeing and chemical technology of textile fibers* (4th Ausg.). London: Charles Griffin & Co. Ltd.

Tutak, M., & Özdemir, M. (2011). Reactive dyeing of cationized cotton: Effects on the dyeing yield and the fastness properties. *J. Appl. Polym. Sci., 119*, 500-504.

Tyndall, R. M. (1990). Upgrading garment washing techniques. *Am. Dyest. Rep., 79*, 22-30.

Tyndall, R. M. (1992). Improving the softness and surface appearance of cotton fabrics and garments by treatment with cellulase enzymes. *Textile Chem. Color., 24*, 23-26.

Tzanov, T., Calafell, M., Gübitz, G., & Cavaco-Paulo, A. (2001). Bio-preparation of cotton fabrics. *Enzyme Microb. Tech., 29*, 357.

Übenacker, M., Lorz, R., Auhorn, A., & Esser, A. (2002). Physikochemische Mechanismen bei der Störstoffbehandlung-Möglichkeiten und Grenzen der messtechnischen Erfassung. *Das Papier-Science and Technology, 1*, 39-45.

Udomkichdecha, W., Kittinaovarat, S., & Potiyaraj, P. (2003). Acrylic and maleic acids in nonformaldehyde durable press finishing of cotton fabric. *Text. Res. J., 73*(5), 401-406.

Vali, S., & Arney, W. (1971). Reaction mechanisms of glyoxal-based durable-press resins with cotton. *Text. Res. J., 41*, 336-338.

Van der Maarl, M., van der Veen, B., Uitedhaag, J., Leemhuis, H., & Dijkhuizen, L. (2002). Properties and applications of starch-converting enzymes of the α-amylase family. *J. Biotechnol., 94*, 137-155.

Vigo, T. (1983). Protection of textiles from biological attacks. In S. Sello, *Functional Finishes: Part A, Chemical processing of fibers and fabrics, Handbook of Fiber Sicence and Technology* (Vol. II, pp. 367-426). New York: Marcel Dekker.

Vorman, I., Lecoeur, E., Bourbigot, S., & Delobel, R. (2004). Guanidine hydrogen phosphate-based flame-retardant formulations for cotton. *J. Ind. Tex., 34*, 27-38.

Vrsalović Presečki, A., Findrik, Z., & Vasić-Rački, Đ. (2009). Starch hydrolysis by the synergistic action of amylase and glucoamylase. *New. Biotechnol., 25*(1), 170.

Wakelyn, P., & Betroniere , N. (2007). *Cotton fiber chemistry and technology.* Boca Raton: CRC Press.

Walker, J., & Kokowicz, S. (1951, April 10). *Patent No. 2,548,455.* United States.

Walsh, G. (2002). *Proteins: biochemistry and biotechnology.* Chichester: John Wiley & Sons.

Wang, C., & Chen, C. (2005). Physical properties of crosslinked cellulose catalyzed with nano titanium dioxide. *J. Appl. Polym. Sci., 97*(6), 2450-2456.

Wang, T., Chen, J., & Chen, C. (2003). Criosslinking of cotton cellulose in presence of alpha-amino acids, part I: physical properties and agent distribution. *Text. Res. J., 73*, 797-801.

Wei, W., Yang, C., & Jiang, Y. (1999). Nonformaldehyde durable press garment finishing of cotton slacks. *Textile Chem. Color., 31*(1), 34-38.

Weil, E. (1992). In R. Engel, *Handbook of organophosphorus chemistry* (pp. 683-738). New York: Marcel Dekker.

Weil, E., & Levchik, S. (2008). FLame retardants in commercial use or development for textiles. *J. Fire. Sci., 28*, 243-281.

Welch, C. (1988). Tetracarboxylic acids as formaldehyde-free durable press fnishing agents. *Text. Res. J., 58*, 480-486.

Welch, C. (1990). Durable press finishing without formaldehyde. *Textile Chem. Color., 22*(5), 13.

Welch, C. (1992). Formaldehyde-free durable press finishes. *Rev. Prog. Color., 22*, 32-41.

Welch, C. (1994). Formaldehyde-free DP finishes with polycarboxylic acids. *Am. Dyest. Rep., 83*(2), 19-26.

Welch, C. (2001). Formaldehyde-free durable press finishing. In M. Pastore, & P. Kiekens, *Surface characteristics of fibers and textiles.* New York: Marcel Dekker.

Welch, C. M., & Andrews, B. A. (1989b, April 11). *Patent No. 4,820,307.* United States.

Welch, C., & Andrews, B. (1989a). Cross-links: a route to high performance nonformaldehyde finishing of cotton. *Textile Chem. Color., 21*(2), 13-17.

Welch, C., & Peter, J. (1997). Mixed polycarboxylic acids and mixed catalysts in formaldehyde-free durable press finishing. *Textile Chem. Color., 29*(3), 22-27.

Whipple, E. (1970). The structure of glyoxal in water. *J. Am. Chem. Soc., 92*, 7183-7186.

Whipple, E., & Ruta, M. (1974). Structure of aqueous glutaraldehyde. *J. Org. Chem., 39*, 1666-1668.

Wieprecht, T., Hazenkamp, M., Rohwer, H., Schlingloff, G., & Xia, J. (2007). Design and application of transition metal catalysts for laundry bleach. *Comptes Rendus Chimie, 10*(4-5), 326-340.

Wilder, G., Nahr, U., Eichhorn, H., & Schindler, W. (1997). Dyeing and printing of basofil fabrics. *Technische Textilien*, 104-105.

Wilkie, C., & Morgan, A. (2010). *Fire retardancy of polymeric materials* (2nd ed.). Boca Roton: CRC Press.

Wood, M. (1992). Fungal cellulases. *Biochem. Soc. Trans., 20*, 46-53.

Wu, W., & Yang, C. (2004). Comparison of DMDHEU and melamine-formaldehyde as the bonding agents for a hydroxyl-functional organophosphorus flame retarding agent on cotton. *J. Fire. Sci., 22*(2), 125-142.

Wu, W., & Yang, C. (2006a). Comparison of different reactive organophosphorus flame retardant agents for cotton: part1: the bonding of the flame retardant agents to cotton. *Polym. Degrad. Stab., 27*, 2541-2548.

Wu, W., & Yang, C. (2007a). Comparison of different reactive organophosphorus flame retardant agents for cotton. Part II: fabric flame resistant performance and physical properties. *Polym. Degrad. Stab., 92*, 363-369.

Wu, W., & Yang, C. Q. (2006b). A comparative study of different organophosphorus flame retardant agents for cotton: Part I: The covalent bonding of the flame retardant agent to cotton. *Polym. Degrad. Stab., 91*(11), 2541-2548.

Wu, W., & Yang, C. Q. (2007b). A comparative study of different organophosphorus flame retardant agents for cotton: Part II: The fabric flammabilty and physical properties. *Polym. Degrad. Stab., 92*(3), 363-369.

Wu, X., & Yang, C. (2008). Flame retardant finishing of cotton fleece fabric: Part III - The combination of maleic acid and sodium hypophosphite. *J. Fire. Sci., 26*, 351-368.

Wu, X., & Yang, C. (2009). Flame retardant finishing of cotton fleece fabric: Part IV - Bifunctional carboxylic acids. *J. Fire. Sci., 27*, 431-446.

Wu, X., Yang, C., & He, Q. (2010). Flame retardant finishing of cotton fleece: part VII. Polycarboxylic acids with different numbers of functional groups. *Cellulose, 17*, 859-870.

Yang, C. (1991a). Characterizing ester crosslinkages in cotton cellulose with FT-IR photoacoustic spectroscopy. *Text. Res. J., 61*, 298-305.

Yang, C. (1991b). FT-IR spectroscopy study of the ester crosslinking mechanism of cotton cellulose. *Text. Res. J., 61*(8), 433-440.

Yang, C. (1993a). Effect of pH on nonformaldehyde durable press finishing of cotton fabric: FT-IR spectroscopy study: part I: ester crosslinking. *Text. Res. J., 63*, 420-430.

Yang, C. (1993b). Effect of pH on nonformaldehyde durable press Finishing of cotton fabric: FT-IR spectroscopy study: part II: formation of the anhydride intermediate. *Text. Res. J., 63*, 706-711.

Yang, C. (1993c). Infrared sopectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. I. Identification of the cyclic anhydride intermediate. *J. Appl. Polym. Sci. Part A: Polym. Chem., 31*, 1187-1193.

Yang, C. (1993d). Infrared spectroscopy studies of the effects of catalysts on the ester crosslinking of cotton cellulose by poycarboxylic acids. *J. Appl. Polym. Sci., 50*, 2047-2053.

Yang, C. (2001). FTIR spectroscopy study of ester crosslinking of cotton cellulose catalyzed by sodium hypophosphite. *Text. Res. J., 71*(3), 201-206.

Yang, C., & Bakshi, G. (1996a). Quantitative analysis of the nonformaldehyde durable press finish on cotton fabric: acid-base titration and infrared spectroscopy. *Text. Res. J., 66*(6), 377-384.

Yang, C., & Kottes Andrews, B. (1991c). Infrared spectroscopic studies of the nonformaldehyde durable press finishing of cotton fabrics by use of polycarboxylic acids. *J. Appl. Polym. Sci., 43*, 1609-1616.

Yang, C., & Lu, Y. (1999). In-situ polymerization of maleic acid and itaconic acid and crosslinking of cotton fabric. *Text. Res. J., 69*(10), 782-789.

Yang, C., & Lu, Y. (2000). In-situ polymerization of maleic acid and itaconic acid on cotton: MALDI/TOF mass spectroscopy and light-scattering study. *Text. Res. J., 70*(4), 359-362.

Yang, C., & Qiu, X. (2007). Flame-retardant finishing of cotton fleece fabrics: part I. the use of a hydroxy-functional organophosphorus oligomer and dimethyloldihydroxylethyleneurea. *Fire Mater, 31*, 67-81.

Yang, C., & Wang, X. (1996b). Formation of cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study. *Text. Res. J., 66*(9), 595-603.

Yang, C., & Wang, X. (1996c). Infrared sepectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids. II. Comparison of different polycarboxylic acids. *J. Polym. Sci., Part A: Polym. Chem., 34*, 1573-1580.

Yang, C., & Wang, X. (1997a). Infrared spectroscopy studies of the cyclic anhydride as the intermediate for the ester crosslinking of cotton cellulose by polycarboxylic acids, III: the molecular weight of a crosslinking agent. *J. Polym. Sci. Polym. Chem., 35*, 557-564.

Yang, C., Wang, X., & Kang, I. (1997b). Ester crosslinking of cotton fabric by polymeric carboxylic acids and citric acid. *Text. Res. J., 67*, 334-342.

Yang, C., Wu, W., & Xu, Y. (2005). The combination of a hydroxy-functional organophosphorus oligomer and melamine-formaldehyde as a flame retarding finishing system for cotton. *Fire Mater, 29*, 109-120.

Yang, C., Xu, L., Li, S., & Jiang, Y. (1998). Nonformaldehyde durable press finishing of cotton fabrics by combining citric acid with polymers of maleic acid. *Text. Res. J., 68*, 457-464.

Yang, H., & Yang, C. (2003). Nonformaldehyde durable flame-retardant finishing of nomex/cotten blend using a hydroxyl-functional organophosphorus oligomer and 1,2,3,4-butanetetracarboxylic acid. *J. Fire. Sci., 25*(5), 425-446.

Yonghua, L., & Hardin, I. (1997). Enzymatic scouring of cotton, effect on structure and properties. *Text. Chem. Color., 29*, 71-76.

Yoon, K., Woo, J., & Seo, Y. (2003). Formaldehyde free cross-linking agents based on maleic anhydride copolymers. *Fiber Polym, 4*(4), 182.

Yu, Y., Lee, E., & Bang, E. (2008). A new catalyst for glyoxal durable press finish of cotton fabrics. *Fiber Polym, 9*(6), 715-719.

Yuen, C., Ku, S., Kan, C., Cheng, Y., Choi, P., & Lam, Y. (2007). Using nano-TiO2 as co-catalyst for improving wrinkle-resistance of cotton fabric. *Surface Rev Lett, 14*(4), 571-575.

Zamocky, M., Regelsberger, G., Jakoptisch, C., & Obinger, C. (2001). The molecular pecularties of catalse – peroxidases. *FEBS Lett., 429*(3), 177-182.

Zeronian, S., & Nevell, T. (1985). *Cellulose chemistry and its applications.* New York: John Wiley & Sons.

Zhang, F., Chen, Y., Lin, H., & Lu, Y. (2007). Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as salt-free dyeing auxiliary. *Color. Technol., 123*, 351-357.

Zhu, P., Sui, S., Wang, B., Sun, K., & Sun, G. (2004). A study of pyrolysis and pyrolysis products of flame retardant cotton fabrics by DSC, TGA and PY-GC-MS. *Anal. Appl. Pyrol.* , 645-655.